RECYCLING POLYISOBUTYLENE CATALYSTS AND POLYMERS

A Dissertation

by

CHRISTOPHER B WATSON

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Chair of Committee,	David E. Bergbreiter
Committee Members,	Melissa Grunlan
	David Powers
	Daniel Singleton
Head of Department,	Simon North

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ABSTRACT

In recent years, the Bergbreiter group has investigated the use of polyisobutylene (PIB) as a selective phase anchor for catalysts and dyes into a nonpolar or alkane solvent phase. The selectivity of these polymeric supports for nonpolar solvents has allowed for separation of catalysts from polar products after reaction by simple extraction with polar solvents. Additionally, the ease with which the PIB chain facilitates separation of homogeneous catalysts from products can also be used to recover and reuse the PIB bound species as well.

This work expands on these ideas of recycling and repurposing PIB. First, PIB was depolymerized by using a trifluoromethanesulfonic acid (triflic) catalyst and an arene solvent. This allowed for the PIB to be converted into *tert*-butyl arenes. This reaction is catalyzed by triflic acid as long as the PIB is suitably end functionalized and there is an available arene solvent to attack the monomer units as they are formed.
The second PIB recycling method was through the use of PIB bound sulfonic acid catalysts that were dissolved into poly(α-olefin) solvents (PAO). This acid/solvent system could be recycled due to its low leaching and low vapor pressure. This work explores the use of this recyclable system in the formation of esters, acetals, and heterocycles. This acid/solvent system was also compatible with a variety of workups including vacuum distillation, filtration, and extraction.

The final PIB recycling method used a PIB bound Rose Bengal catalyst in PAOs that could be recycled due to its phase selectivity. Although this catalyst did suffer from

photo bleaching, we hypothesize that additional care with storage and reaction conditions could allow this PIB bound catalyst to be recycled multiple times.

The following work will discuss these three recyclable systems for PIB in further detail.

DEDICATION

This dissertation is dedicated to my mother and father who always pushed me to be better, and to my wife who has supported me throughout graduate school.

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First, I would like to thank my Ph.D. advisor, Dr. David E. Bergbreiter for his guidance, support, and patience during my studies. I consider myself lucky to have worked in his group as he was a better mentor and teacher than I could have hoped for. I would also like to thank Dr. Melissa Grunlan, Dr. David Powers, and Dr. Daniel Singleton for their willingness to serve on my committee. I would further like to thank Jill Powers and Angie Tieken Medina for their assistance throughout my time here. Sandy Manning Horton and Valerie McLaughlin also deserve special thanks for their immense help both as guides during graduate school and as friends that supported me during my studies.

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Contributors

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The TGA measurements of PIB bound acids were conducted by Angelo Kirchon. Studies of PIB depolymerization in Chapter 2 were conducted in part by Dustin Tan. Studies of PIB bound sulfonic acids in Chapter 3 were conducted in part by Adrianna Kuechle. Studies of PIB bound Rose Bengal were conducted in part by Peyton Young.

All other work conducted for the dissertation was completed by the student independently.

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NOMENCLATURE

ADMET	Acylclic diene metathesis
Da	Daltons
DCM	Dichloromethane
GPC	Gel permeation chromatography
H_2SO_4	Sulfuric acid
HDPE	High density polyethylene
LLDPE	Linear low density polyethylene
LDPE	Low density polyethylene
NMP	Nitroxide mediated polymerization
PEG	Poly(ethylene glycol)
PAO	Poly(α-olefin)
PE	Polyethylene
PIB	Polyisobutylene
PPG	Polypropylene glycol
PPM	Parts per million
$T_{ceiling}$	Ceiling Temperature
THF	Tetrahydrofuran
Triflic	Trifluoromethane sulfonic
UHMWPE	Ultra high molecular weight polyethylene

TABLE OF CONTENTS

Page

ABSTRACT ii

DEDICATION iv

ACKNOWLEDGEMENTS v

CONTRIBUTORS AND FUNDING SOURCES vii

NOMENCLATURE viii

TABLE OF CONTENTS ix

LIST OF FIGURES xi

LIST OF TABLES xvii

LIST OF EQUATIONS xviii

CHAPTER I INTRODUCTION 1

- Polyolefins 2
- Polymer End Groups 15
- Polyisobutylene Uses 25
- Olefin Oligomeric Solvents 33

CHAPTER II ENTHALPICALLY DRIVEN POLYISOBUTYLENE DEPOLYMERIZATION 42

- Introduction 42
- Results and Discussion 58
- Conclusion 83

CHAPTER III PIB BOUND SULFONIC ACIDS IN PAOS, A RECYCLABLE CATALYST/SOLVENT SYSTEM.. 85

- Introduction 85
- Results and Discussion 98
- Conclusion 114

CHAPTER IV STUDIES ON THE RECYCLABILITY OF PIB BOUND ROSE BENGAL......116

Introduction......116
Results and Discussion......120
Conclusion......128

CHAPTER V EXPERIMENTAL......130

General Experimental......130
Syntheses and Experimental Procedures......130

CHAPTER VI CONCLUSION......144

REFERENCES......148

LIST OF FIGURES

Page

Figure I-1 Generalized conversion of ethanol to ethylene and water................................1

Figure I-2 Generalized renewable formation of isobutylene from ethanol........................2

Figure I-3 Low MW PE used for soft coloring materials and UHMWPE used as body armor..3

Figure I-4 Radical abstraction of a hydrogen atom leading to a butyl sidechain..............4

Figure I-5 General mechanism for the Ziegler-Natta polymerization of polyethylene......5

Figure I-6 The Philips heterogeneous catalyst for polymerization of PE 6

Figure I-7 Visual representation of the three most common forms of PE: HDPE, LLDPE and LDPE 7

Figure I-8 A: Isotactic PE, B) Syndiotactic PE, C) Atactic PE...9

Figure I-9 Transition states leading to a. Syndiotactic and b. Isotactic polypropylene ...10

Figure I-10: General mechanism for olefin metathesis...12

Figure I-11 Polymerization of bicyclo[2.2.1]hept-2-ene via ring opening metathesis 14

Figure I-12 Introduction and Alteration of Polymer End Groups.. 16

Figure I-13 Chain transfer from polyethylene to a monomer 17

Figure I-14 Chain termination via disproportion or recombination................................17

Figure I-15 Generalized versions of the three most common caps for controlled radical polymerization. 18

Figure I-16 PE polymerization yielding a highly active magnesium end group that can be further converted into thiols in a variety of ways. 19

Figure I-17 A typical example of an acetal copolymer..20

Figure I-18 Stylized polymer grafting example 20

Figure I-19 PIB bound Grubbs catalyst for improved nonpolar solubility 21

Figure I-20 Crosslinked polystyrene sulfonate is used to exchange sodium ions for calcium ions. 22

Figure I-21 Reaction of Ytterbium Salt catalyst bound to crosslinked polystyrene bead 23

Figure I-22 Generic overview of Merrifield Resins, which can be further modified. 24

Figure I-23 Cationic PIB growth from isobutylene 25

Figure I-24 Examples of PIB End group alterations by Kennedy et. al. 26

Figure I-25 Alterations of PIB end groups by Storey et. al. 27

Figure I-26 BASF breakdown of PIB uses at differing molecular weights as Oppanol^{TM} 29

Figure I-27 Synthetic routes from PIB alkene to several different end groups 31

Figure I-28 Examples of PIB bound Grubbs Catalysts from our group 32

Figure I-29 Removal of heptane from heptane/water mixture (a) mixtures of PIB$_{2300}$ bound catechol magnetic oil in heptane and water. (b) The magnetic heptane layer was trapped by a magnetic force.. 32

Figure I-30 PIB bound IBX analog 33

Figure I-31 PEG as a recyclable solvent for palladium catalyzed coupling. 34

Figure I-32 Improved separation of PE bound catalyst from Polymer product by addition of Polywax. 35

Figure I-33 PE bound porphyrin dye that was removed from product via addition of unfunctionalized PE 36

Figure I-34 Visualization of the anti-leaching effect of PIB$_{2300}$... 37

Figure I-35 PIB bound para-methyl red isomerization was found to occur at the same rate in both heptane and PAO. 38

Figure I-36 PAOs are shown to be highly nonflammable in comparison to the more traditional hexane 39

Figure I-37 PAOs extracting benzene from contaminated water. 40

Figure I-38 Product isolation methods from PAOs 41

Figure II-1 (Top) Products formed after partial pyrolysis of PIB_{9000} at 400 °C for 10 seconds and (Bottom) expansion of the GPC spectra for the higher molecular weight oligomers showing multiple similar products......................44

Figure II-2 Predominant mechanism of degradation proceeds to form the isobutylene equivalents. 46

Figure II-3 At 300 °C, the volatilized material from the PIB degradations is linearly dependent on time. 46

Figure II-4 Random chain scission by cumyloxy radical to give the stable ether, preventing depolymerization. 48

Figure II-5 (Left set of spectra) The IR spectra changes over 2300 hours for the photo-oxidation of PIB under a mercury lamp and air at 35 °C. (Right set of spectra) The IR spectra rising over 350 hours for the photo-oxidation products of PIB under a mercury lamp and air at 90 °C. 49

Figure II-6 Decrease in molecular weight of the PIB chains as function of gamma dosage in three different solvents.. 50

Figure II-7 The log of the molecular weight for 3 virgin samples (V1, V2, V3) that had been irradiated with 0, 9, and 57 kGy total dose... 51

Figure II-8 Change in molecular weight and total number of chains of PIB over time during turbulent flow. 52

Figure II-9 Decoupling of coupled PIB by hetero lytic cleavage... 54

Figure II-10 Summary of previous observations within our group. 56

Figure II-11 Mechanism for acid catalyzed exchange of phenol end group for anisole end group 57

Figure II-12 The degree of PIB_{1000} alkene degradation calculated by comparing the ratio of singlet of the generated *tert*-butyl arene relative to the remaining PIB methylene peak using ^{1}H NMR spectroscopy. 60

Figure II-13 Synthetic routes to different end functionalized PIB_{1000} oligomers. 61

Figure II-14 Degree of PIB_{1000} degradation for different end groups calculated by comparing the ratio of singlet of the generated *tert*-butyltoluene relative to the remaining PIB methylene peak using NMR Spectroscopy 63

Figure II-15 GPC spectrum of products for 1 g of PIB_{1000} alkene depolymerization over time with 1 equivalent of triflic acid in 6 mL of benzene at 0 ^{o}C. 66

Figure II-16 Rearrangements that could convert the tertiary 2,4,4-trimethyl carbocation 1 into a structurally isomeric 2,3,4-trimethylpentyl tertiary carbocation 4 that could form the minor product 1,1,2,3-tetramethylbutylbenzene.......67

Figure II-17 GPC spectrum of products for 1 g of PIB_{1000} alkene depolymerization over time with 2 equivalent of triflic acid in 6 mL of benzene at 0 ^{o}C. 68

Figure II-18 GPC trace of PIB_{1000} with different end groups in the presence of benzene (dotted) or toluene (solid) and 11 equivalents of triflic acid at room temperature after 20 hours.......70

Figure II-19 Possible intermediates of functionalized PIB in presence of triflic acid. 71

Figure II-20 GPC trace of PIB alkene after degradation using 2 equivalents of triflic acid and stated solvent after 20 hours.......73

Figure II-21 Depolymerization of 1 g PIB_{1000} alkene using 2 equivalents of triflic acid in 60 mL of benzene over time.......75

Figure II-22 Depolymerization of 1 g PIB_{1000} alkene using 2 equivalents of triflic acid in 60 mL of toluene over time. 76

Figure II-23 Depolymerization of 1 g PIB_{1000} using 2.2 equivalents of triflic acid in either 0.1 or 0.2 equivalents of benzene at room temperature.......78

Figure II-24 GPC trace of three different molecular weights of PIB degrading in the presence of 2.2 equivalents of triflic acid and 60 mL of benzene after 20 hours at room temperature.......79

Figure III-1 First step in the synthesis of Ibuprofen, catalyzed by recycled HF.......86

Figure III-2 Camphorsulfonic acid catalyzed synthesis of coumarin derivative in 5 mL of ethanol:water.......87

Figure III-3 BAIL catalyzed acetylation of 30 mmol of glycerol with 1500 mmol of acetone to give 92-96% conversion to the ketal. 88

Figure III-4 Amberlyst resin catalyzed synthesis of dodecyl phenol.......89

Figure III-5 Amberlyst resin catalyzed synthesis of *tert*-butyl methyl ether. 89

Figure III-6 Amberlyst catalyzed formation of sulfone products. 90

Figure III-7 PEG-OSO_3H catalyzed conversion using 1 mmol of aldehyde and 10 mmol acetic anhydride to form acetic acetals.......90

Figure III-8 Synthesis of sulfonic acid modified PMO *in-situ* or in a two-step process.. 91

Figure III-9 Cellulose-OSO_3H (13 mol%) catalyzed Nazarov-cyclization reaction of 1 mmol of a dieneone in 10 mL of ethanol that can be recycled at least 5 times........92

Figure III-10 Use of Nafion-H resin in ethanol to catalyze multicomponent condensation reactions........93

Figure III-11 Palladium catalyzed Suzuki coupling in 2 grams of PEG_{400} solvent at 110 °C. 96

Figure III-12 Synthesis of alkyl and aryl PIB bound sulfonic acids 2 and 3. 99

Figure III-13 TGA analysis plot of PIB-bound sulfonic acid 2 showing no desulfonation prior to depolymerization........101

Figure III-14 TGA analysis plot of PIB-bound aromatic sulfonic acid 3 showing no desulfonation prior to depolymerization........102

Figure III-15 (far left) *p*-Methyl red 4 dissolved into methanol above a PAO_{432} phase while, (second from left) *p*-methyl red 4 dissolved into methanol with methanesulfonic acid above a PAO_{432}, (second from right) *p*-methyl red 4 dissolved into methanol above a PAO_{432} phase containing 2 and (right) *p*-methyl red 4 dissolved into methanol above a PAO_{432} phase containing 3....103

Figure III-16 Conversion of the protections of benzyl alcohol with dihydropyran was tested in recycling experiments with dodecylbenzenesulfonic acid, 2, and 3.105

Figure III-17 PIB bound acids 2 and 3 in PAO_{423} are effective catalysts for the dihydropyran protection of benzyl alcohol and can be recycled 10 times without noticeable lost in yield or contamination of the product by catalyst or solvent. 106

Figure III-18 Multicomponent reaction of 2 mmol of benzaldehyde, 3 mmol of urea, 2 mmol of ethyl acetoacetate in 10 mL of PAO_{432} catalyzed by either 2 or 3 at 90 °C. 107

Figure III-19 Comparison of kinetics for esterification of propionic acid with benzyl alcohol using 2 or 3 in PAO_{432}, or *p*-toluenesulfonic acid in toluene at 70 °C. 110

Figure III-20 Esterification of hexanoic acid and methanol in PAO_{432} at 70 °C using 1 mol% of either 2 or 3........114

Figure IV-1 Conversion of 8-oxoG to Spiroiminodihydantoin using PTT to generate singlet oxygen 117

Figure IV-2 Some photosensitizers dyes 117

Figure IV-3 Use of Rose Bengal in the final step of the total synthesis of Dysidiolide.118

Figure IV-4 Use of Eosin Y as a photocatalyst for the oxidation of phosphines to phosphine oxides. 118

Figure IV-5 Methylene Blue generated $^1O_2$ converts phenol to hydroquinone and benzoquinone. 119

Figure IV-6 Synthesis of PIB bound Rose Bengal 121

Figure IV-7 (Left) PIB bound Rose Bengal dissolved into heptane above a layer of 80% ethanol: 20% water. 122

Figure IV-8 PIB bound Rose Bengal 7 catalyzed conversion of terpinene to ascaridole in heptane using1) a flask open to air 2) an air balloon 3) an O_2 balloon 4) air through a dispersion tube. 123

Figure IV-9 Rate of PIB bound Rose Bengal 7 catalyzed conversion of terpinene to ascaridole in solvents of different polarities. 125

Figure IV-10 Rate of PIB bound Rose Bengal 7 catalyzed conversion of terpinene to ascaridole in PAOs of different molecular weights. 126

LIST OF TABLES

Page

Table III-1 Molecular weights and flash points of various PAOs....................................97

Table III-2 Alcohol to ester conversions using catalyst 2 in PAO_{423} at 70 °C with calculated theoretical conversions in parentheses. 111

Table III-3 Alcohol to ester conversions using catalyst 3 in PAO_{423} at 70 °C with calculated theoretical conversions in parentheses. 111

Table IV-1 Conversions of terpinene to ascaridole in various recycled solvents. 127

LIST OF EQUATIONS

Page

Equation I-1 Gibbs free energy equation at constant pressure..12

Equation II-1 Calculation of ΔH using the heats of formation of starting materials and products..82

Equation II-2 Calculation of ΔH using the difference in energy between isobutylene polymerizing and isobutylene being attacked by benzene to give *tert*-butylbenzene. 82

Equation II-3 Calculation of ΔH using the difference between the heat of formation of *tert*-butylbenzene, benzene, isobutylene and an approximation of heat of polymerization all in the gas phase. 82

Equation III-1 Calculation of ΔH using heats of formation for alcohol, acids, esters, and water..112

Equation III-2 Approximation of ΔG as ΔH assuming that the TΔS term is small. 112

Equation III-3 Equation for calculating an equilibrium constant from ΔG. 112

Equation III-4 Equation for calculating Keq from equilibrium concentrations. 112

Equation III-5 Equation for calculating equilibrium concentration of the product ester from an equilibrium constant..112

Equation V-1 Equation to calculate the conversion of polymer to depolymerization products..131

CHAPTER I

INTRODUCTION

Polyolefins are ubiquitous materials. They are commercially made on large scale with molecular weights that vary from 400 to over 1,000,000 Da. Methods for their synthesis and ways they can be used in various applications are a major industrial chemistry activity. As materials, their use and their eventual disposal broadly impacts society. These polymers are most commonly made from fossil fuel derived alkenes by various types of polymerization reactions. In some cases, the alkenes can be derived from more sustainable sources. For example, the monomer for the synthesis of polyethylene (PE), ethylene, can be derived from bioethanol (Figure I-1) though the economics of this process vary depending on the availability and cost of petroleum in a given market. This process has recently seen commercial success in the form of Braskem's I'm Green™ Polyethylene which makes bio based PE from sugarcane derived ethanol.[1] This can be achieved using a host of different catalysts such as phosphoric acids, metal oxides, and molecular sieve catalysts.[2,3]

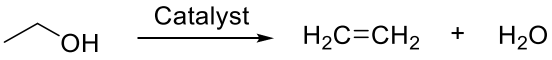

Figure I-1 Generalized conversion of ethanol to ethylene and water

Likewise, polyisobutylene (PIB), can be derived from these fossil fuel based feedstocks, by fractionation of natural gas and subsequent dehydrogenation of isobutane followed by polymerization of the isobutylene monomer. Isobutylene can also be derived from renewable resources. For instance, there has been some promise in the renewable formation of isobutylene via acid catalyzed dehydration of fermented isobutanol or the catalytic conversion of ethanol into isobutylene via multistep processes (Figure I-2).[4,5] Enzymatic catalysis, while normally considered a more boutique type of catalysis, is already used on a large scale in the production of fructose from starch. Enzymatic catalysis is also an active area of study for synthesis of biofeedstocks. Thus it is encouraging to note that isobutylene can also be formed from 3-hydroxy-3-methylbuterate by Saccharomyces cerevisiae mevalonate diphosphate decarboxylase.[6]

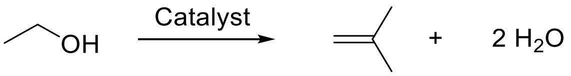

Figure I-2 Generalized renewable formation of isobutylene from ethanol

However, while this process has the potential for making renewably sourced polyisobutylene; it is not yet the most common or economically viable option.[7]

Polyolefins

The polyolefins prepared from these starting materials have found far ranging uses. Products like synthetic rubber, fuel additives, the ubiquitous packaging materials encountered on a daily basis, fibers, plastic bags, clothing, and bullet-proof vests are some of the many ways these materials are used. There are also less common applications of more academic interest. These would include using polyolefins as solvents and catalyst supports, work pioneered by our group. These are just a few of the thousands of applications of polyolefins. [8,9,10]

One of the most commonly used polyolefins today is PE, but even materials, that all have the formula C_nH_{2n}, produced from the ethylene monomer, can be highly varied. In the simplest variable, the molecular weight of the polymer can be varied, which greatly changes the properties of the product polymer. For instance, shorter oligomers of polyethylene, those less than 1000 Daltons (da), like Polywax, can be used to make waxy materials such as crayons, while ultra-high molecular weight PE (UHMWPE), which has a M_n greater than 1 million Da, is a much tougher material and can be used for things such as plastic butchers blocks or even as body armor (Figure I-3).

Figure I-3 Low MW PE used for soft coloring materials and UHMWPE used as body armor

A key difference between these materials is just the molecular weight. This can reflect the feed ratio of the monomers and catalyst or initiator which is the simplest way to control the molecular weight. The MW however is also affected by the actual chemistry involved in the polymerization. For example, MW can also be controlled by control of termination events such as eliminations or radical recombination. These events can be controlled by choice of polymerization chemistry. For instance, switching from free radical polymerization to cationic polymerization can help to avoid active chain combination which terminates chain growth, leading to larger and less branched chains.

Moving away from radical polymerization can also have a large effect on the type of PE that is produced. This is because it helps to avoid the intra-molecular abstraction of a hydrogen radical to form small side chains that are typically butyl groups. These groups are the most common defect in radical polymerization because they involve hydrogen abstraction via a relatively stable 6 membered transition state. Although less common, the pathway on the right (Figure I-4) can also occur, which leads to the formation of ethyl side chains. This chemistry is commonly seen in the processes leading to the formation of low density polyethylene (LDPE). This LDPE is still useful however for things such as cling film wraps or plastic bags.

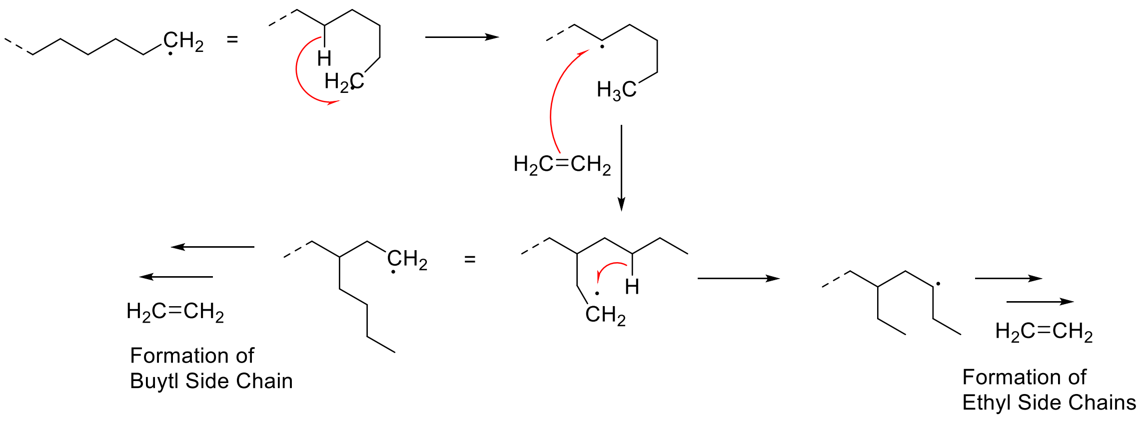

Figure I-4 Radical abstraction of a hydrogen atom leading to a butyl sidechain

Originally, polyethylene was prepared by a radical high pressure process. This formed low density polymer that was the only useful polyolefin until Karl Ziegler and Giulio Natta developed transition metal catalyzed syntheses of high density polyethylene (HDPE) and stereoregular polypropylene (PP). The importance of this chemistry is evidenced by the Nobel Prize awarded to Ziegler and Nata in 1963 "for their discoveries in the field of the chemistry and technology of high polymers."[11]

Given the importance of these polyolefins, there has been considerable effort to understand the mechanisms of their synthesis. Figure I-5 illustrates some of the elementary coordination and insertion steps that are thought to be involved in Ziegler-Natta polymerization

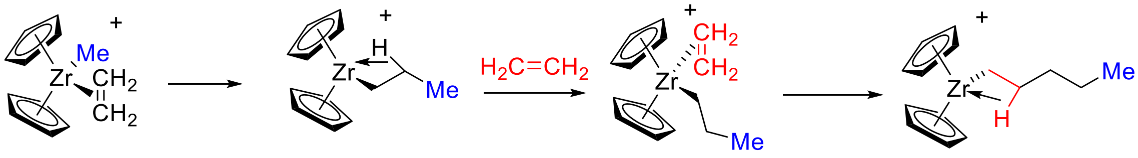

Figure I-5 General mechanism for the Ziegler-Natta polymerization of polyethylene.

This less branched polymer, produced by Ziegler-Natta chemistry allowed for a drastic change in molecular weight and physical properties of polyethylene. Because of the reduced number of branches, HDPE is composed of more linear chains that have improved packing of the chains themselves. This leads to more crystalline regions in the bulk material and thus a higher strength to density ratio. This improved packing also leads to a higher melting point and also makes the bulk material more opaque than the

LDPE. This makes it excellent for uses such as piping, due to its nearly nonexistent leaching and high resistance to most solvents. It is also commonly used in jugs, bottles, and is a leading material used in the making of many plastic toys.

There are other catalysts that are used for the industrial formation of PE. One of these is the Philips catalyst, which is a chromium silicon oxide catalyst (Figure I-6). This catalyst is responsible for between 40-50% of the world's HDPE production.[13] The key difference between the Ziegler-Natta type catalysts and this Philips catalysts other than the obvious differences in metal center and ligands is that the Philips catalyst is supported on silica gel, rather than being a stand-alone catalyst.

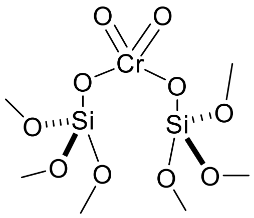

Figure I-6 The Philips heterogeneous catalyst for polymerization of PE

The three most common types of PE are HDPE, LDPE, and linear low density PE (LLDPE) (Figure I-7). As their names imply, the distinctions between these types of polyolefins are partially based on density, with HDPE being greater than 0.941 g/cm^3, LDPE being between 0.910 and 0.940 g/cm^3, and LLDPE being more narrowly 0.915-0.925 g/cm^3. While the processes for making these materials vary widely, the largest difference between the LDPE and LLDPE, is in fact, LLDPE is not truly PE at all. It is made as a copolymer between PE and short α-olefins like 1-butene, 1-hexene, and 1-

octene. These copolymers allow for the formation of materials similar to LDPE, however because the chains remain linear, the control of MW is easier as is the reproducibility and uniformity of the materials. This increased linearity coupled with shorter side branches allows LLDPE to make thinner films than traditional LDPE. This is because the LLDPE chains are better able to slide past each other during the elongation process than the larger branched LDPE chains. LLDPE also has higher tensile strength and impact resistance than LDPE.

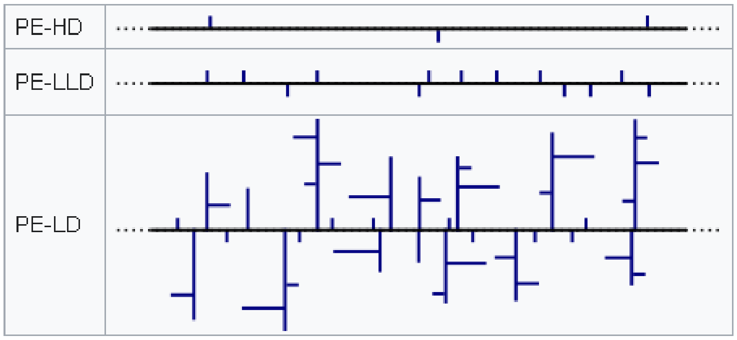

Figure I-7 Visual representation of the three most common forms of PE: HDPE, LLDPE and LDPE

Blends of these materials can also be made. In these cases, the materials, such as LDPE and LLDPE are made separately and then blended together to give materials of the desired properties. For instance, blown films of LLDPE are often blended with LDPE to improve melt strength. This can however decrease the toughness of the final material.[14] However, there are limitations on mixing different polymers and LDPE and HDPE and PE made from C_2D_4 are not completely miscible with PE made from C_2H_4.

While PE is overall a very resilient material it is simply an alkane. As a result, it is relatively unreactive and not biodegradable. This has led to problems with its disposal. For instance, in 2010 nearly 690,000 tons of HDPE were produced, but less than 5% of that amount was recycled.[15] This recycling is commonly done by isolating the HDPE from other materials, cleaning it an then shredding it. After shredding it is melted down and formed into pellets that can then be reused in industrial processes to remake HDPE products.

While recycling the PE is promising, it is also of interest to biodegrade PE. To address this, there has been considerable work on its biodegradability in addition to its recycling. For instance, the bacterium Brevibacillus borstelensis has been found to use PE as a carbon source at 50°C.[16] Additionally, it has been found that Indian meal moth larvae (*Plodia interpunctella*) are capable of both metabolizing and partially degrading shorter chain oligomers of PE. [17] Overall this is promising work toward returning at least some forms of PE to the carbon cycle.

The next simplest, and also one of the most commonly used Poly(α-olefin)s is polypropylene (PP). PP is similar to PE in its resistance to solvents and other forms of corrosion, but is generally a stronger, stiffer and higher melting material. The synthesis for polypropylene is most commonly accomplished using with either a Ziegler-Natta type catalyst or with a metallocene catalyst, depending on the desired tacticity. This tacticity, which is the arrangement of the methyl groups relative to each other, is the most important feature of PP (Figure I-8).

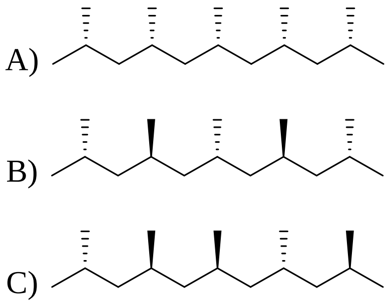

Figure I-8 A: Isotactic PE, B) Syndiotactic PE, C) Atactic PE

The tacticity of the polymer is a function of the type of catalyst used to make the polymer as well as the ligands on the catalyst itself. While control of tacticity is a very complex subject, there are simplistic ways to visualize how tacticity can be controlled. For instance in Figure I-9 below, the transition state for addition of a monomer can be used to understand how tacticity can be controlled. In the first example (a), the transition state leading to addition of a monomer to the growing polymer chain has the methyl group of the incoming propylene unit pointed down to minimize steric hindrance from the methyl on the growing chain, which leads to an alternating (Syndiotactic) pattern. In the second example (b), a large Y ligand is introduced. The steric hindrance from this group leads to the methyl group on the propylene unit pointing up which further leads to an isotactic propylene pattern. In the absence of either of these driving forces, or if they roughly balance out, a random (atactic) distribution will be formed.

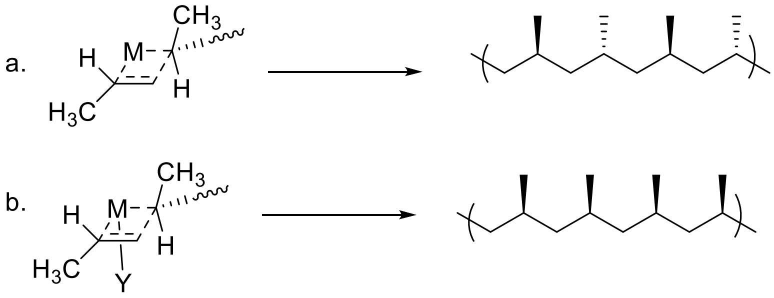

Figure I-9 Transition states leading to a. Syndiotactic and b. Isotactic polypropylene

While these molecules may seem similar, the small difference of the methyl group direction has a vast influence on the properties of the materials. For instance, atactic PP is an amorphous polymer with minimal crystalline regions due to its poor packing and order. This leads to it being tacky and rubber like, while having a lower melting point than other forms of PP. In contrast, Isotactic PP has a higher melting point and is a much more durable material. This is why the vast majority of marketed PP is the isotactic version. This isotactic version is also ideal for injection molding due to its reasonable ~170 °C melting point.

PP is used in a large variety of materials. One relevant example is the use of PP for medical and laboratory supplies as it has a high enough melting point to be able to be used in an autoclave, (which is too high a temperature for most PE). PP is also ideal for hinges, as it is highly fatigue resistant, especially when the polymer chains are oriented over a hinge. Because of its high solvent resistance, PP is also commonly used in piping and plumbing systems. A final example is the rolling of PP into sheets that allow for it to be used for things like plastic folders.

Copolymers of PE and PP are also extraordinarily common. While the feed ratios of the two materials can have drastic effects on the properties of the product, in general, the products are still very chemical resistant, can be used in an autoclave like PP, but still maintain much of the flexibility offered by traditional PE. These materials thus find significant use in laboratory glassware as a more shatter resistant material that is still cleanable in an autoclave.[18] These materials also find electrical uses as the outer coating to wires due to their poor conductance.

Still other metal catalyzed processes such as ring-opening metathesis polymerizations have been developed as a route to polyolefins. This process, whose simplified mechanism is shown in Figure I-10, also received recognition in 2005 when Yves Chauvin, Roberg H. Grubbs, and Richard R. Schrock received their Nobel Prizes for “the development of the metathesis method in organic synthesis.”[19,20] A version of this process called the ADMET process developed by the Wagener group is an alternative route to branched polyethylenes.

Figure I-10 shows the steps that are involved olefin metathesis polymerization. A similar set of steps that use α,ω-dienes are involved in another metathesis based polymerization process. In that case, the reaction is an equilibrium that produces ethylene and the polymerization reaction is driven by Le Chatelier’s Principle via the bubbling off the ethylene as it is formed. This process is known as acyclic diene metathesis (ADMET) polymerization.

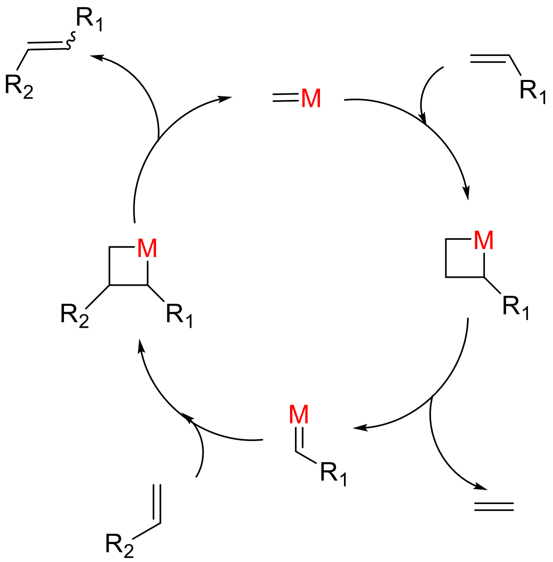

Figure I-10: General mechanism for olefin metathesis[21]

In addition to these reactions cationic, anionic, free and controlled radical polymerizations can be used to make some polyolefins. The work described in later chapters is focused on the use of the polyolefin polyisobutylene (PIB) which is primarily made via cationic polymerization of isobutylene using some form of either Lewis acid catalyst or even through simple Brønsted-Lowry acid catalysis.

The success of any chemical process, including these polymerization reactions, is predicted by the Gibb's equation (Equation I-1):

$$\mathbf{\Delta G = \Delta H - T\Delta S}$$

Equation I-1 Gibbs free energy equation at constant pressure

This thermodynamic relationship predicts that a polymerization reaction is at least fundamentally possible as long as the ΔG is negative. While it does not predict the rate of this process, it is critical in that it shows that the polymerization reaction has to be driven by a negative ΔH, positive ΔS, or some combination of the two. Given that the polymerization reaction is inherently entropically challenged, the ΔS is usually negative and the –TΔS term is net positive. This means that the reaction is usually driven by a favorable negative ΔH.

For example, in the case of ethylene polymerization or the cationic polymerization of isobutylene a π-bond becomes a σ-bond. This leads to a negative ΔH because σ-bonds are stronger than π-bonds and thus more energetically favored. In other cases, like the ring opening metathesis polymerization of bicyclo[2.2.1]hept-2-ene (Figure I-11), the bonds in the products are essentially the same as the starting materials, so other effects drive the polymerization. In the absence of any other effect, the starting materials or oligomers and high molecular weight polymer would simply be at equilibrium. However, bicyclo[2.2.1]hept-2-ene is a strained cycloalkene. Thus, by releasing this strain the ring opening process releases enough ΔH to account for the net loss of entropy. Another illustrative example of this ring strain requirement would be that cyclobutene readily polymerizes but cyclohexene does not. This is due to the much larger strain of the cyclobutene ring compared to the nearly strainless cyclohexene ring. Other metathesis reactions, such as the ADMET process, are driven by the removal of ethylene following Le Chatelier's Principle.

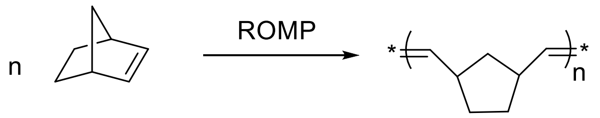

Figure I-11 Polymerization of bicyclo[2.2.1]hept-2-ene via ring opening metathesis

The cationic polymerization of alkenes such as isobutylene to make polyisobutylene (PIB) also illustrates the importance of a negative ΔH. In this case, as was noted for ethylene, polymerization is driven by the conversion of C-C π bonds to C-C σ bonds which are lower in energy by approximately 340 kJ/mole. This large negative enthalpy change makes up for the large loss of entropy that comes from turning many molecules into one molecule. The relative stability of the generated tertiary carbocation also helps to make this reaction facile in addition to the total process being energetically favorable.

A key issue with any polymerization is that the TΔS term for the equation is temperature dependent and most often unfavorable. Thus there is a temperature at which polymerization reactions will no longer be thermodynamically favorable. At this temperature, known as the ceiling temperature ($T_{ceiling}$), the entropy term in the Gibbs equation cancels out the favorable enthalpy term. At any temperature above this, the ΔG is positive and the reaction is thermodynamically unfavorable. The $T_{ceiling}$ is thus the temperature above which the polymerization reverses and the polymer chain depolymerizes back to reform individual monomer units. This $T_{ceiling}$ value will vary based on not only the polymer type, but also on the degree of polymerization, as differing degrees of polymerization can limit the degrees of freedom in different ways, especially as the polymer begins to fold back onto itself.

This $T\Delta S$ term also leads to a balancing act when synthesizing polymers. The temperature must be low enough for the polymer to form (i.e. below $T_{ceiling}$), but it also must still be high enough for the reaction to proceed at a reasonable rate. If the temperature is dropped too low, the average monomer could have less energy than the activation energy of the reaction. At this point, the reaction would not be able to proceed at an acceptable rate, despite being thermodynamically favorable because it would be kinetically too slow.

Polymer End Groups

With the exception of cyclic polymers, all polymers have end groups. The identity of these end groups vary depending on the mechanism of termination of a polymerization reaction and subsequent chemistry can be used to alter this group. In general, the identity of end groups depends on one of three approaches: use of a functional initiator to give a functional end group, *in situ* termination to introduce an end group, and post polymerization modification (Figure I-12).[22]

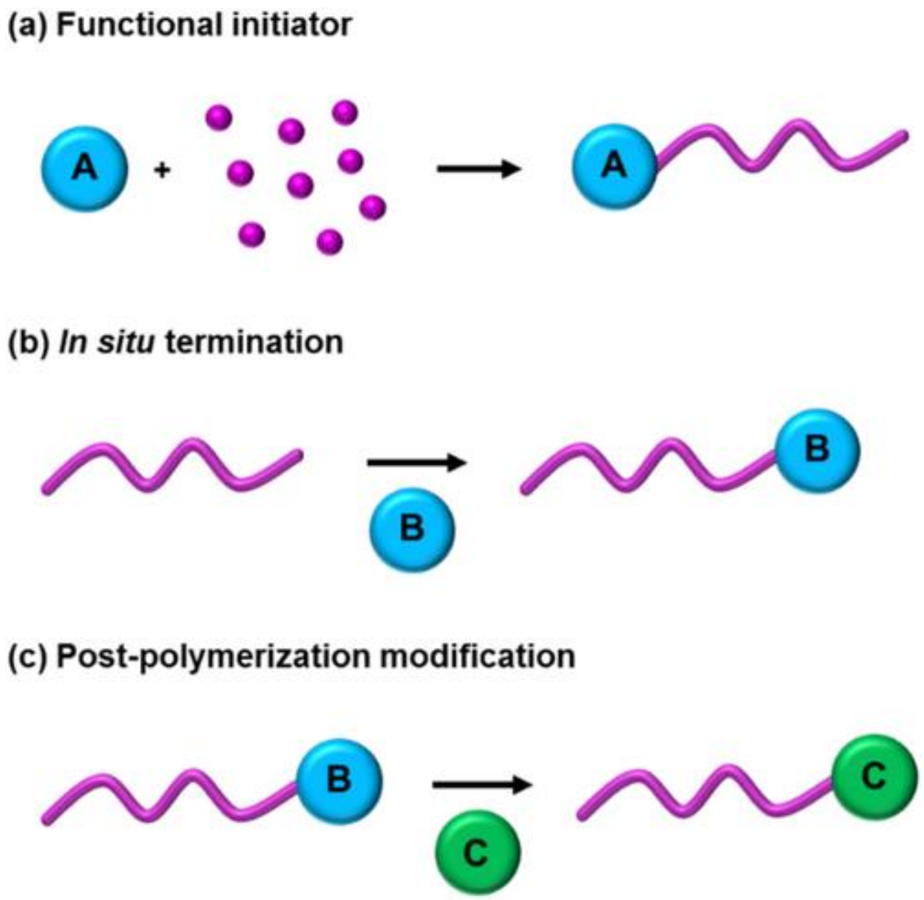

Figure I-12 Introduction and Alteration of Polymer End Groups. Reprinted with permission from (22).

Radical reactions, for instance, terminate in the absence of other species by chain transfer, recombination, or disproportionation (Figure I-13 and Figure I-14). Although this kind of termination can be good for making highly stable polymers, this lack of functionality can be problematic when it comes to functionalizing polymers for other uses.

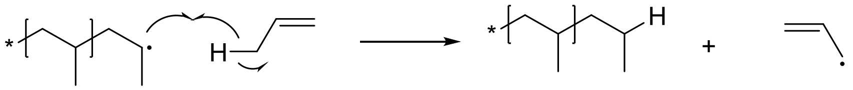

Figure I-13 **Chain transfer from polyethylene to a monomer**

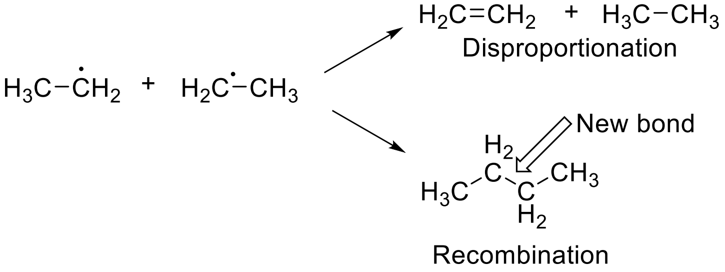

Figure I-14 **Chain termination via disproportion or recombination**

Controlled radical polymerizations, would be an example where the initiating and terminating groups can be varied to control the chemistry of a polymer's end group. The three most common types of these are atom transfer radical polymerization (ATRP), reversible addition-fragmentation chain transfer polymerization (RAFT), and nitroxide-mediated radical polymerization (NMP) (Figure I-15). Although the groups used to cap the chain differ, fundamentally, they all work to suppress free radicals in order to prevent recombination, allowing for controlled chain growth. They also have the added bonus of terminated the polymer itself in a functional group which allows for much easier modification of the polymer after the initial polymerization.

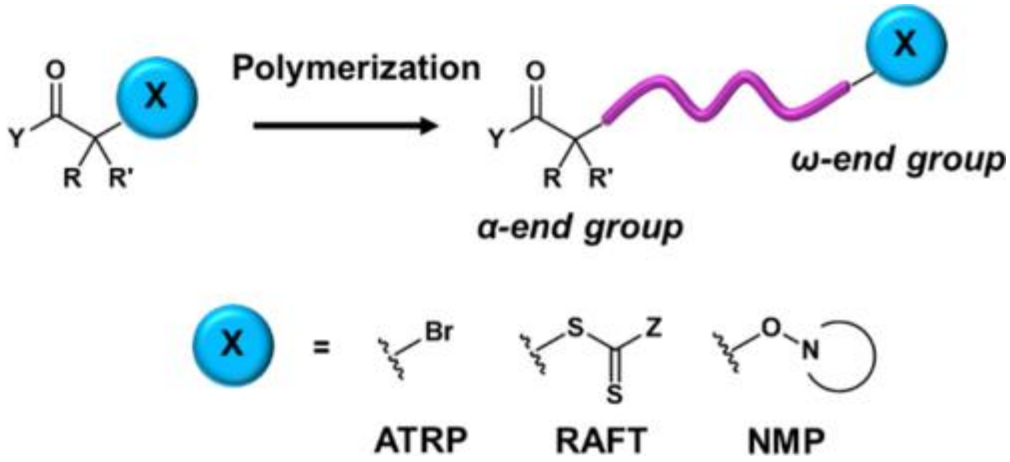

Figure I-15 Generalized versions of the three most common caps for controlled radical polymerization. Reprinted with permission from (22)

The Ziegler-Natta polymerizations discussed earlier are most commonly terminated by β-hydride elimination or by deliberate introduction of H_2 to limit polymer size which can lead to alkene and alkene end groups. These polymerizations can also be terminated via the deliberate addition of O_2 to the reaction vessel allowing for chain end oxidation. A similar termination can also be accomplished by the addition of CO_2.

Other methods have also been developed to introduce chain terminated in other functional groups. For instance, Boisson, et. al. have developed polyethylene polymerization conditions using a neodymium lithium catalyst along with treatment with a butyl-octyl-magnesium species to turn the PE generated into a Grignard species.[23] This highly active end group can then be used to convert the PE end group to a wide variety of functionality. This is illustrated in Figure 16, where thiols are introduced onto PE in a variety of ways (Figure I-16).

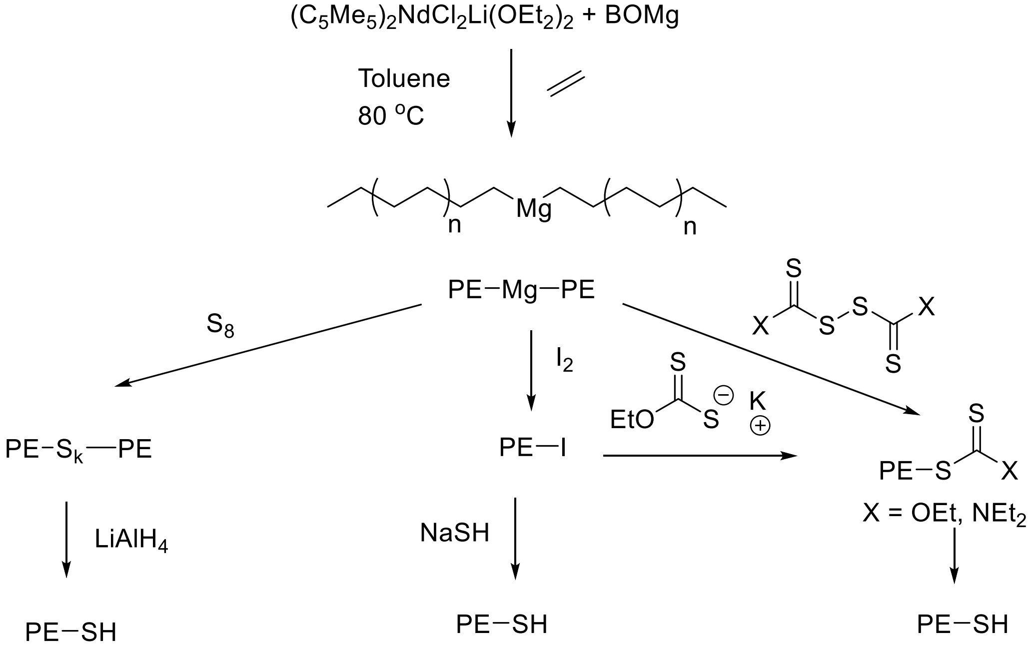

Figure I-16 PE polymerization yielding a highly active magnesium end group that can be further converted into thiols in a variety of ways.

In some applications, the identity of the end group of the polymer is especially useful. With lower molecular weight materials, it can change a polymer's properties. For example surfactants, such as soap, can go from being a near water insoluble oligomer, to being soluble due to its ionic end group forming micellar structures, which effectively hide the nonpolar tail from the surrounding solution.

Another example of these groups being especially important is with polyacetals (PAs). These polymers initially found minimal use because of their low ceiling temperatures, which allowed for depolymerizations at elevated or even ambient temperatures. However, their physical properties can be greatly enhanced by end capping them with an ester rather than the far more reactive alcohol (Figure I-17).[24]

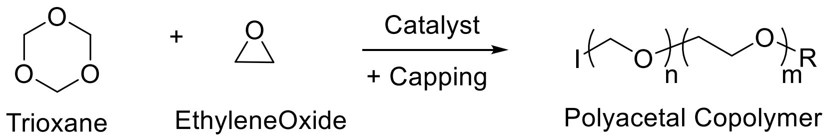

Figure I-17 A typical example of an acetal copolymer.

This change is so important because the depolymerization mechanism proceeds by reversal that liberates an aldehyde and a new alcohol on a chain that is one monomer shorter. This process is prevented by having the alcohol attack something like an anhydride to generate an ester. This ester is far less electron rich and thus far less likely to deplolymerize.

Alternatively, end groups can allow for further functionalization of the polymer. For example, end groups can be used for grafting chemistry whereby a functional group terminated polymer is attached to another group either via attack of or by its functional group (Figure I-18).

Figure I-18 Stylized polymer grafting example

Examples of this from our group include grafting onto polyolefins via alkylborane intermediates.[25] Our group has also used end groups to make diblock copolymers of PIB and acrylate oligomers.[26] In our group, end groups are routinely used to prepare phase separable and recyclable catalysts such as PIB bound Grubbs catalyst (Figure I-19) that can then be recycled into via extraction into the nonpolar phase.[27,28]

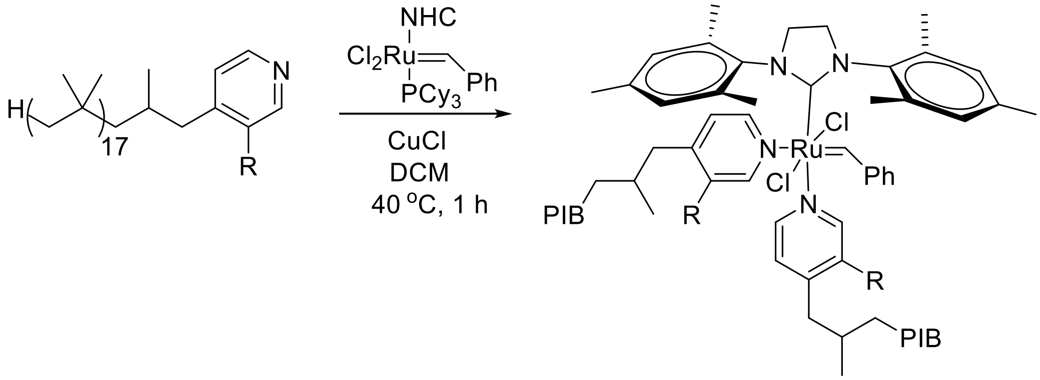

Figure I-19 PIB bound Grubbs catalyst for improved nonpolar solubility

The end group functionalization of polyolefins, while important in its own right, is a process that if broadly important in polymer chemistry. Some polymers, for example are unstable without such chemistry. Polyacetals formed 1,3,5-trioxane or formaldehyde have hydroxymethyl end groups and spontaneously depolymerize in acid or base because the they are simply acetals. They thus require end groups designed to prevent polymer degradation. In the case of Delrin this involves an esterification. In the case of Celcon ethylene oxide is used to form a copolymer with formaldehyde. The product is then allowed to depolymerize to form stable $–CH_2CH_2OH$ end groups. For different reasons poly(ethylene glycol)'s (PEG) end groups are often modified to graft this polymer onto surfaces to make them more biocompatible.[29] PEG is often attached to drugs via its end group to make otherwise insoluble drugs more bioavailable as the PEG is highly water soluble.

While terminal functionalization can be introduced at the end of a polymerization reaction or the identity of terminal functional groups can be changed after the reaction, polymers can also be functionalized in the main chain in a variety of post-polymerization chemistry. This sort of process can be used to introduce functionality that would normally be incompatible with the polymerization conditions. For example, solid supports such as polystyrene beads are often used to immobilize reagents, substrates, or catalysts.[30] Post polymerization functionalization of these materials was originally introduced in the 1930s are a way to prepare ion exchange resins[31] such as via sulfonation of aromatic rings to form polystyrene beads with sulfonic aid or sulfonate groups. These bound sulfonates have been used extensively as ion exchange resins for removal of ions such as calcium, potassium and sodium (Figure I-20). This process is often used for water softening by trading out the hard calcium in water for softer sodium ions.

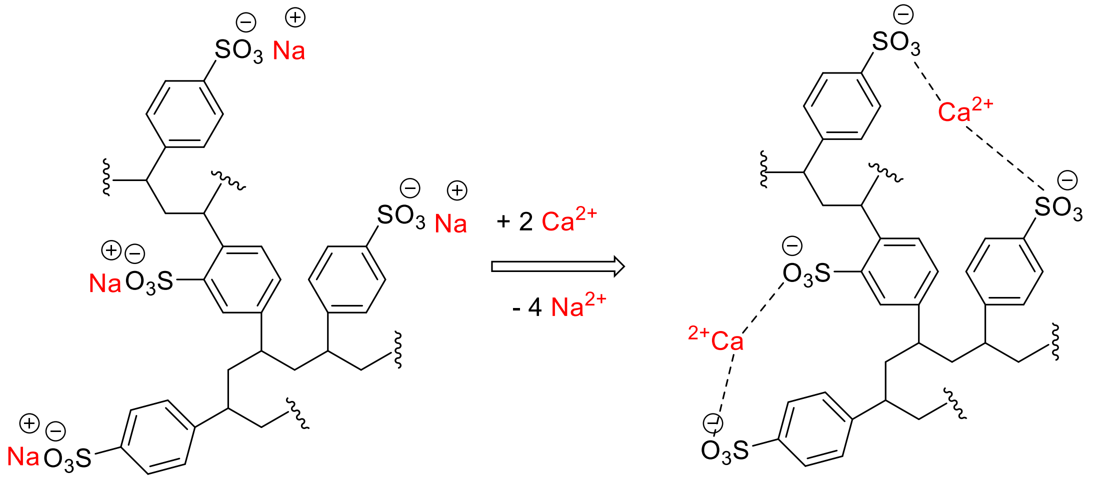

Figure I-20 Crosslinked polystyrene sulfonate is used to exchange sodium ions for calcium ions.[32]

Such chemistry has subsequently been used to make polymer bound catalysts. For example, sulfonic acid containing polystyrenes and their salts are used as heterogeneous catalysts in reactions such as multicomponent reactions with ytterbium salts (Figure I-21).[33]

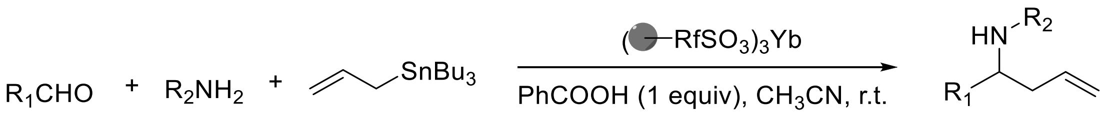

Figure I-21 Reaction of Ytterbium Salt catalyst bound to crosslinked polystyrene bead

Removable acid catalysts have been used in reactions such as benzylation of toluene using benzyl alcohol, isomerization reactions,[34] and have also been used for esterification of fatty acids.[35] The fuel additive tert-butyl methyl ether can be made using these recyclable acid catalysts. The importance of this chemistry is that the arylsulfonic acid group is the equivalent of sulfuric acid in these reactions. however, since the sulfonic acid groups are covalently attached to polystyrene, a physical separation allows for simple removal of the sulfonic acid catalyst after the reaction. Typically this is accomplished using simple filtration.

The post polymerization of crosslinked insoluble polystyrene for synthesis and catalysis received even more attention after Merrifield’s pioneering work in 1960 that showed how these modified polymers could be used in peptide synthesis via iterative coupling and deprotection reactions which lead to rapid and nearly quantitative creation of desired amino acid sequences with facile separation and purification of the immobilized intermediates. That work, which led to Merrifield being awarded a Nobel Prize in 1984, is another example of post polymerization modification (Figure I-22).

This led to literally 1000s of reports describing versions of these stoichiometric syntheses. It also led to many papers discussing phase separable homogeneous catalysts, work that continues to be important and receive attention today.[36,37]

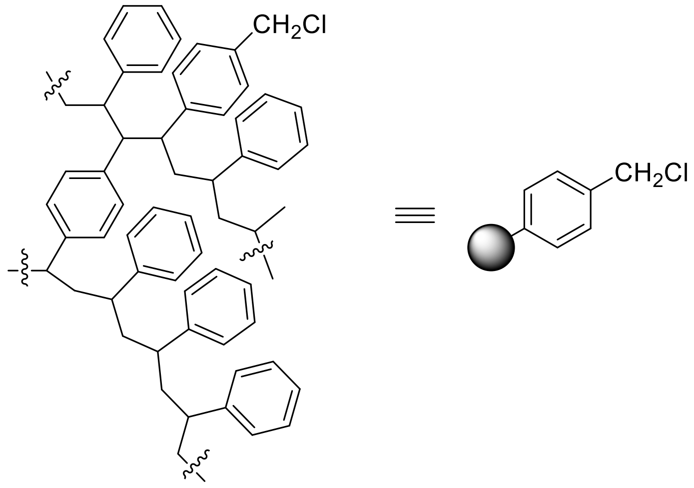

Figure I-22 Generic overview of Merrifield Resins, which can be further modified.

A final example of post polymerization modification would be the oxidation of polymer surfaces. This chemistry is of interest as a way to alter how a polymer interacts with its environment without changing the polymers intrinsic properties such as its tensile strength, its permeability, or its thermal stability. A simple example of this would be the oxidation of polyethylene surfaces to alter polyethylene's wettability. This can be accomplished in varying ways using polyethylene insoluble oxidants like chromic acid, corona discharge treatments or even simple schemes like flame treating in polyethylene milk jugs. The polar group introduced onto a polyethylene surface can alter its wettability. Such changes are important in a variety of problems ranging from changing biocompatibility to changing the printability by allowing water soluble inks to adhere to a surface.

Polyisobutylene Uses

Polyisobutylene has been a polymer of particular interest in our group, mostly as an agent to control solubility of catalysts or nanoparticles or as a phase anchor to separate catalysts from products after a reaction. Ongoing work suggests it may have other utility as a leaching inhibitor or as a cosolvent. Regardless of the specific application, the polyisobutylene used in this chemistry is material that is made from isobutene via a cationic polymerization of isobutylene, typically at low temperatures. This cationic polymerization is proceeds via initial formation of a tertiary carbocation formed via the protonation of isobutylene. Subsequent additions of isobutylene form new carbocations from the dimer, trimer, tetramer, and oligomers as it grows into a polymer (Figure I-23). The potential reversibility of this process under different conditions will be discussed in a later chapter.

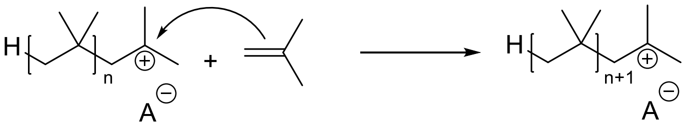

Figure I-23 Cationic PIB growth from isobutylene

The lowered temperature helps to prevent side reactions or chain transfers that could cause non-living behavior for the polymer growth, which allows for relatively controlled polymer dispersity. In addition to these effects, the low temperature, often less than -100 ^{o}C, helps to minimize the impact of the TΔS term of the Gibb's equation. In these polymerizations the negative ΔH of converting π to σ bonds is sufficient to make the polymerization reaction thermodynamically feasible at least at lowered temperatures. For this polymer, it is especially important to avoid high temperatures as the $T_{ceiling}$ for this reaction is only about 170 ^{o}C.[38]

For decades, there has been interest in finding ways to control the end groups of these PIB polymers. For instance Joseph Kennedy was making two and three arm telechelic polymers of PIB anisole, phenol, or PIB carboxylic acids in the 1980's (Figure I-24).[39] These polymers could then be further functionalized via the active phenol end or grafted onto other molecules via an ether linkage.

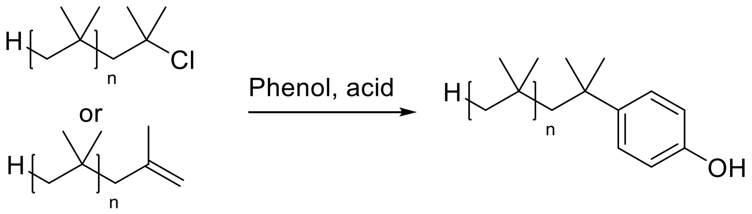

Figure I-24 Examples of PIB End group alterations by Kennedy et. al.

There has also been work on making PIB with reliable chloride and anhydride end groups for purposes of increasing grafting ability as well as other reactivity.[40] More recently, Robson Storey, has investigate PIB with preferential termination as an internal alkene rather than the more common external alkene for purposes of studying PIB fracturing using Lewis Acids. He has also done work making tertiary chloride end groups that were subsequently converted to alkoxy benzenes (Figure I-25).[41]

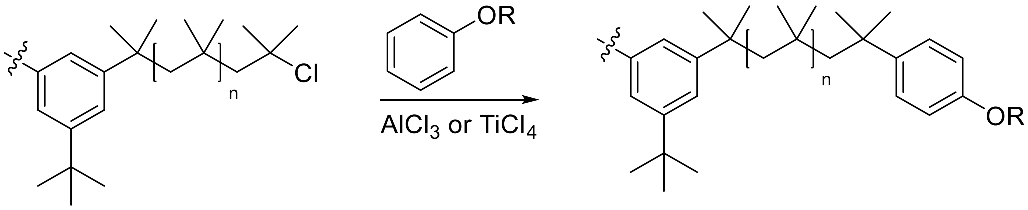

Figure I-25 Alterations of PIB end groups by Storey et. al.

All of this interest helps to show that while the end groups of the polymer itself may only account for a small percentage of the overall molecule, the importance of polymer end groups cannot be overstated. This is especially true when it comes to materials science, as the end groups of the polymers being used for either grafting or crosslinking can have an enormous effect on the overall properties of the material if not properly controlled. These end groups can also open up possibilities for new and interesting chemistry with the polymers themselves, such as attachment of azides which allow for click chemistry or other potentially powerful grafting techniques.

PIB has found use both industrially in applications as a homopolymer as well as in PIB copolymers. Lower molecular weight PIB is used as an additive in fuels and as a lubricant in engines, as its low $T_{ceiling}$ allows it to be converted into isobutylene at combustion and burned off, preventing engine fouling while lubricating. At higher molecular weights, PIB can also be used in sealants and adhesives. It is also sold under the trade name Lubrizol as a viscosity modifier, used for its “shear stability, cleanliness, and thickening ability."[42] PIB has found such common use that its global production is expected to exceed 1.5 million tons by 2024.[43]

The polyisobutylene polymers are commercially prepared in a wide range of molecular weights (Figure I-26). High molecular weight PIB is the most common PIB used for industrial purposes.[44] It is used throughout the automotive and sealant industry for a variety of properties including its heat resistance, oxidation characteristics, and especially its virtual impermeability to gasses as well as water. It also has found growing uses in electronics. This is due to its relatively low density and flexibility, making it ideal for uses in wiring, especially given that it is nonconducting. These high molecular weight polymers have also found use in roofing shingles due to their low water permeability and also their low temperature flexibility (cold flow). Companies such as BASF also are increasingly using it in adhesive applications for a variety of reasons including: high adhesion and tack, good resistance to water solutions of chemicals, low electrical conductivity, and lack of skin irritation. Importantly, it is permitted for food contact such as in packaging due to its lack of toxicity and low bioavailability. These properties also allow for the use of PIB in chewing gum. An informative breakdown of the change in properties as a function of molecular weight is also given for PIB made by BASF under trade name Oppanol™.[45]

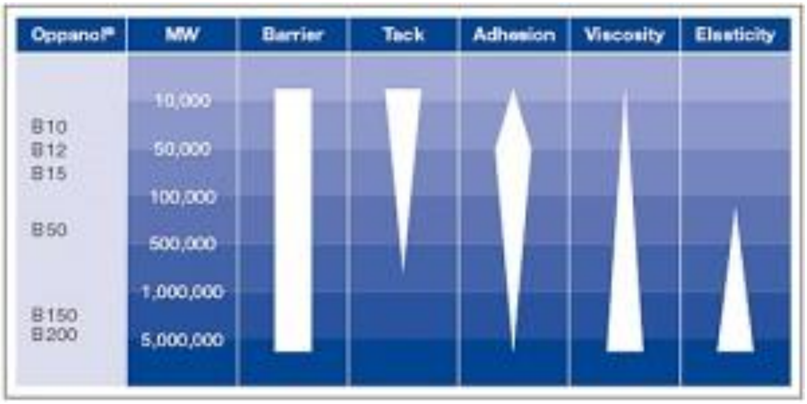

Figure I-26 BASF breakdown of PIB uses at differing molecular weights as Oppanol^{TM}

Low molecular weight PIB has found other interesting uses. It is used largely as a fuel additive, lubricant and viscosity modifier. It is found to be ideal for these uses do to its ability to be slowly flowing which can allow for lubrication. This property has also become of interest for its uses in self-healing surfaces as the polymer can freely flow back into defects of the surfaces. It also finds uses as a sealant, in pressure adhesives, in stretch films, and even as a medical plaster due to its very low toxicity.[46]

PIB's other common use industrially is as a copolymer. A particularly important application is PIB's use in butyl rubber where it makes up approximately 98% of the polymer with the remainder being isoprene. This compound has found wide uses ranging from construction (as an agent to increase durability in concrete), to tires and bladders for sporting balls (due to very poor gas permittivity), and even to healthcare because of supremely low leaching into water.[47] It even has applications as a binder in plastic explosives such as C-4. Due to its lack of general functionality as well as its low permittivity, butyl rubber finds uses as gas masks and chemical protection agent. This lack of functionality leaves the rubber nearly immune to chemical warfare as its surface is nearly unreactive. While still being more rigid than natural rubber, it is still flexible enough to form air tight seals.

In a research setting, especially within our group, PIB has been used as a functional oligomer for many purposes. We have shown numerous methods for end group functionalization, whereby PIB could be used as a nonpolar analog of polyethylene glycol for functionalization purposes.[48] It should be noted that 1 (Figure I-27), and thus its subsequent products, is contaminated with the fully hydrogenated PIB alkane.

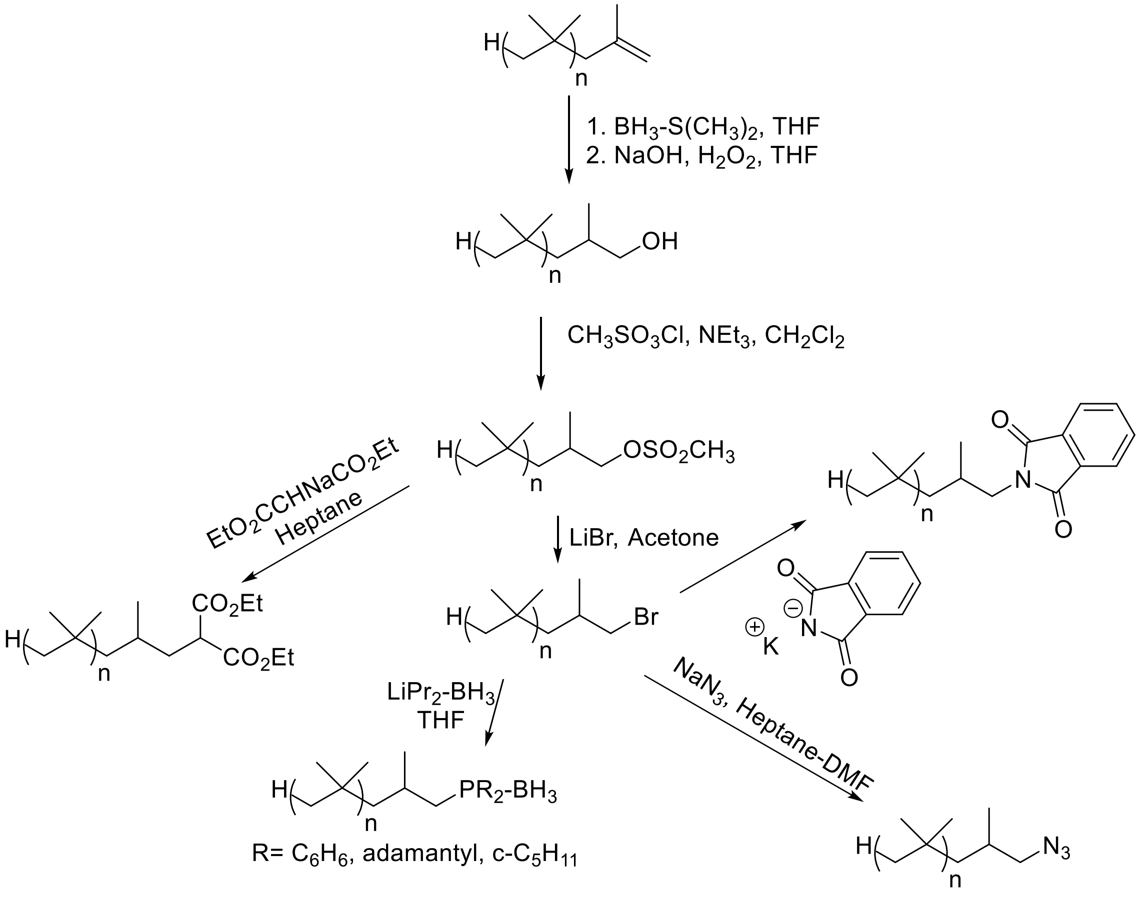

Figure I-27 Synthetic routes from PIB alkene to several different end groups

PIB can also be used as a recovery agent for catalysis such as with Grubbs' metathesis catalyst (Figure I-28).[49] In this application, a PIB bound ligand allowed for recovery and reusability of >98% of the ruthenium used for the reaction. The NHC bound PIB expectedly showed better recovery of the catalyst, as the ether moiety is transient in the active species of the catalyst, while the NHC remains firmly bound throughout the reaction.

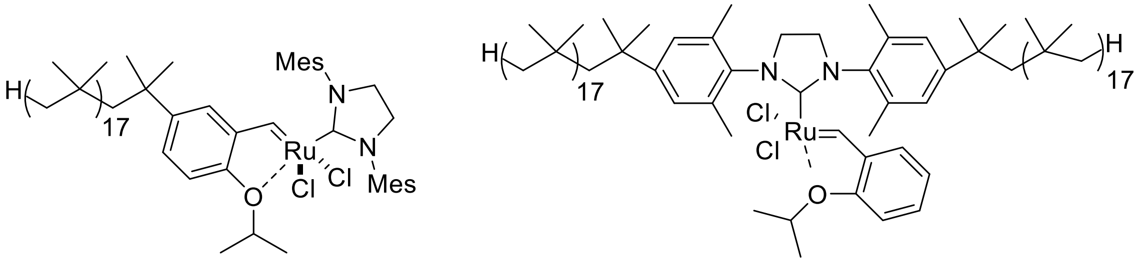

Figure I-28 Examples of PIB bound Grubbs Catalysts from our group[50]

This recoverability chemistry in particular has promise for uses in homogeneous catalysis, as it prevents the leaching of catalysts or catalysts residues into products. PIB has also been used as a solubilizing agent for things such as nanoparticles. One example of this is the solubilization of magnetic nanoparticles (Figure I-29). A recent paper described how such PIB-grafted materials can be used to separate oil from water, in effect making hydrocarbon like heptane act like it was magnetically susceptible.[51]

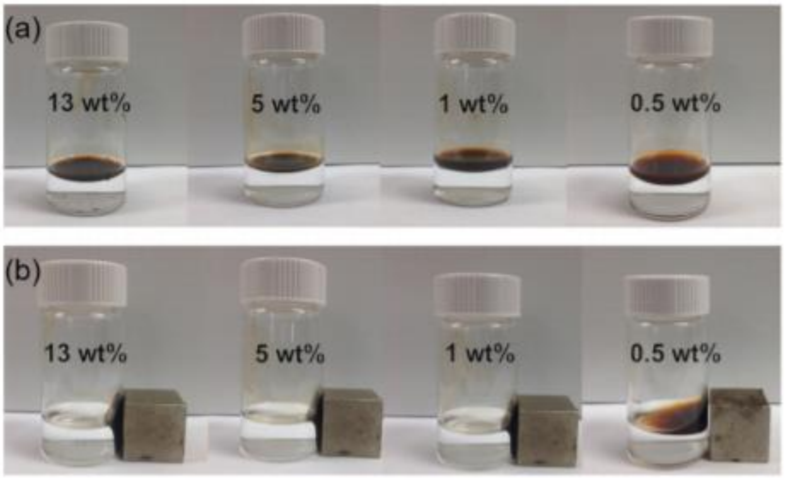

Figure I-29 Removal of heptane from heptane/water mixture (a) mixtures of PIB_{2300} bound catechol magnetic oil in heptane and water. (b) The magnetic heptane layer was trapped by a magnetic force. Reprinted with permission from (51).

PIB has also been used as a recovery agent for organic reagents within our group.[53] It has been used to recover oxidizing agents such as this IBX analog (Figure I-30):

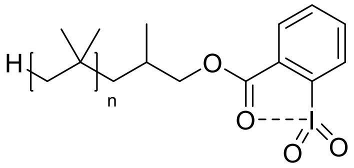

Figure I-30 PIB bound IBX analog

which was used to oxidize alcohols to ketones before being regenerated via a terminal oxidant and reused.

Olefin Oligomeric Solvents

A more recent use for shorter chain polyolefin oligomers has been their use as a solvent. This is of particular interest as a greener process, as these oligomers tend to have much higher boiling points, which can lead to them being more reusable as their lower volatility prevents losses due to evaporation or accidental boiling. Some of the polymers that have been used for this purpose include melted polyethylene, polyethylene glycol (PEG), polypropylene glycol (PPG) and more recently by our group, PAOs.

All of these polymer solvents have some significant advantages over many traditional solvents that serve to make them much greener to use. Most notably, they have a significantly higher MW than conventional solvents and are non-volatile. This property can serve as a significant bonus when attempting to reuse the solvents themselves as evaporation becomes a nearly nonexistent issue. This is especially beneficial when running reactions at elevated temperatures or in open air environments. Additionally, these solvents have very low LD_{50} values (a measure of toxicity measured in grams of chemical needed to harm 50% of test subjects per kilogram of test subject). For instance, PEG_{400} has an approximate LD_{50} of 12.9 g/kg in mice, while the PAOs used in our group have an LD_{50} <5 g/kg, which is significantly lower than a traditional solvent like dichloromethane, which has an LF_{50} of 2 mg/kg.

Polyethers such as PEG and PPG are the most commonly used polymeric solvents. They have been used as solvent in an assortment of catalyzed processes. In most cases, the subsequent products are separated from the PEG by an extraction process (Figure I-31)[54], Higher molecular weight PEG solvents are often precipitated with excess diethyl ether. These processes still pose significant problems in terms of usability and waste generation.

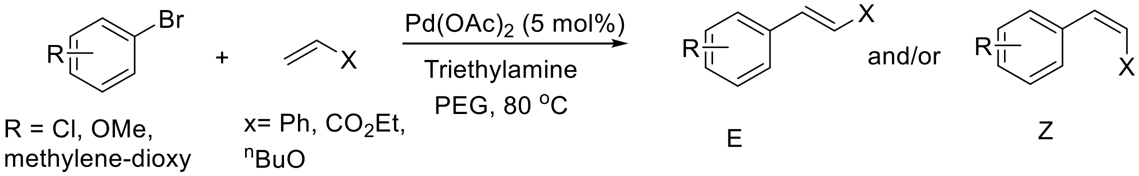

Figure I-31 PEG as a recyclable solvent for palladium catalyzed coupling.

The Bergbreiter group has worked extensively using polyolefins as oligomeric solvents. In one example, polyethylene Figure I-32) was used as a replacement for conventional alkane solvent like heptane for a variety of reactions including ring closing metathesis reactions. This work showed that a molten PE phase is useful as a selective solubilizing solvent as demonstrated by the use of a poly(dodecyl styrene) bound dansyl dye, polyisobutylene bound azo dye, and polyisobutylene or PE bound oligomeric catalysts each of which were selectively soluble in an oligomeric polyethylene solvent phase.[55] Jakkit Suriboot of the Bergbreiter group further showed that PE bound ruthenium catalysts could be used for polymerization, and that the addition of unfunctionalized PE as a solvent allowed for improved separation of the ruthenium catalyst from the polymeric products (Figure I-32).[56] Related work by Dupont with PE oligomer-bound dyes includes excess PE to facilitate separation of a PE-porphyrin bound catalyst from the product material (Figure I-33).[57]

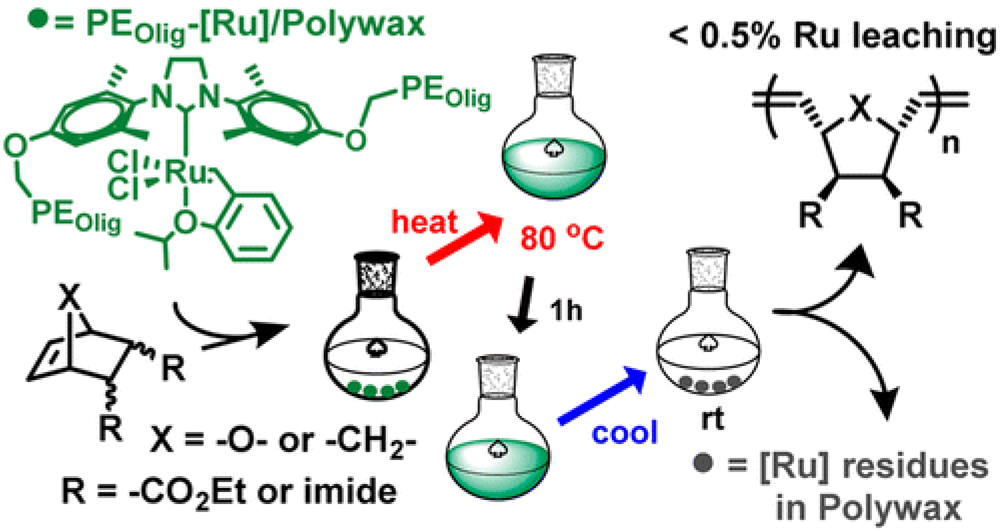

Figure I-32 Improved separation of PE bound catalyst from Polymer product by addition of Polywax. Reprinted with permission from (55).

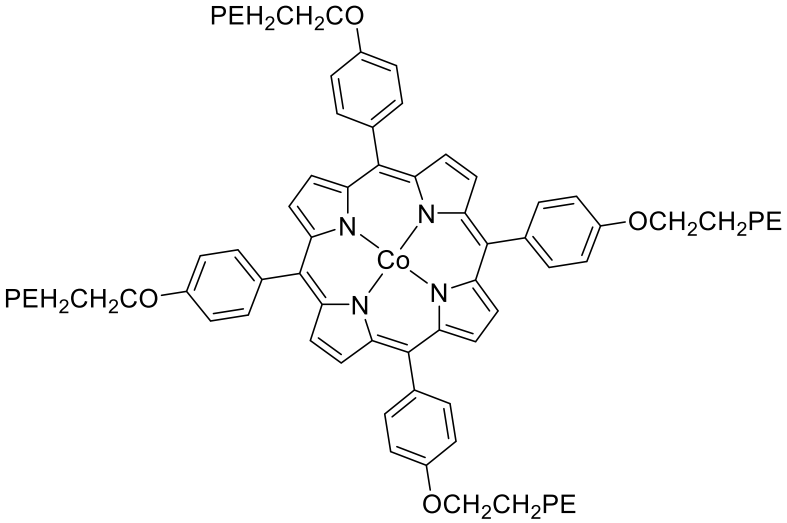

Figure I-33 PE bound porphyrin dye that was removed from product via addition of unfunctionalized PE

Another example out of the Bergbreiter group of the use of polyolefins as solvents or cosolvents is the use of PIB an anti-leaching additive in homogeneous catalytic reactions that used a PIB bound Rh catalyst in a heptane rich solution. This anti-leaching effect, coupled with the already good phase selectivity of PIB bound Rh catalyst helped to facilitate the desired cyclopropanation. In this particular example, the PIB bound catalyst's phase selective solubility in a heptane phase containing some PIB cosolvent suppresses the undesired dimerization product from the ethyl diazoacetate reagent. This paper speculated that this reduction in dimerization product yield arose from improving the phase selectivity of the catalyst. Since ethyl diazoacetate was selectively soluble in the acetonitrile phase of this biphasic reaction, this decrease in concentration of the polymeric catalyst in the acetonitrile phase where the ethyl diazoacetate resides helped to prevent dimerization (Figure I-34).[58]

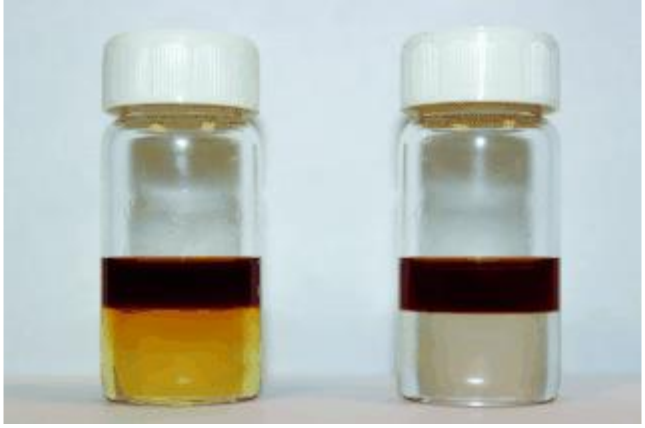

Figure I-34 Visualization of the anti-leaching effect of PIB_{2300}. In a heptane/ethanol/DMF solvent system, PIB bound ruthenium bipyridine has partial leaching into polar phase (left). In the same solvent system, with addition of PIB_{2300} cosolvent, the leaching of the PIB bound ruthenium is greatly decreased (right). Reprinted with permission from (57).

This work where PIB was added as a solvent suggested liquid polyolefins could be used as a solvent just as molten PE was used as a solvent in work described above. Moreover, it suggested that polyolefins that are liquids at room temperature or at sub-ambient conditions too could be used. However, PIB is remarkably viscous-too viscous to be used as the principle component of a solvent. This led our group to explore the use of PAOs as the entire solvent phase. The general idea is that these materials alone or as cosolvents would be alternatives to conventional alkane solvents like hexane or heptane. Some notable results from the initial study of these solvents included the observation that PAOs leach significantly less than the smaller heptane molecules into polar solvents. This study also showed that PAOs used as a solvent for a reaction was practical. Specifically, this study showed that when a polymer bound dye was allowed to isomerize, the rates for these isomerization reactions in these PAO solvents were comparable to the rates in traditional heptane (Figure I-35). Another interesting result from this work was that the rate of this isomerization was the observation that in a carboxylic acid catalyzed isomerization of the same azo dye, that the rate of this isomerization was proportional to the square of the acid catalyst concentration. This suggested that due to the highly nonpolar nature of these solvents, the acids formed dimers at much lower concentrations than with other solvents. This suggested that some reactions in these nonpolar solvents that involve H-bonding or proton transfer could be interesting due to the lack of competition of these hydrocarbon solvents for H-bonding of a protic catalyst.

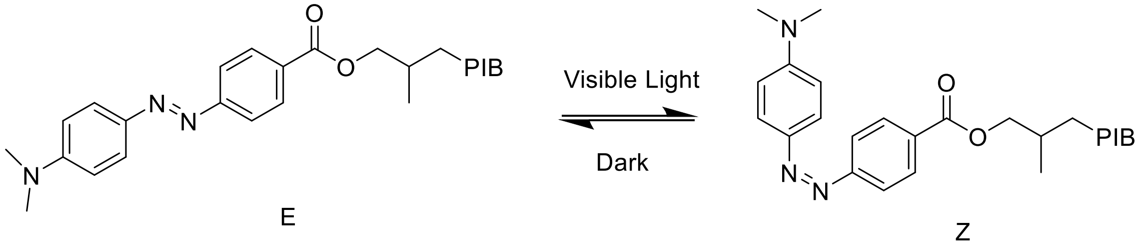

Figure I-35 PIB bound para-methyl red isomerization was found to occur at the same rate in both heptane and PAO.

Another interesting result recently from the Bergbreiter group showed that the high flash point of PAO solvents could be used to reduce the fire hazard of using some pyrophoric organometallic reagents. Malinski and Bergbreiter demonstrated that not only were otherwise highly reactive lithium reagents stable in these solvents, but the solvents themselves served to greatly reduce the flammability of the solution, due to their high flashpoint.[59] In contrast to the conventional pyrophoric hexane solutions of lithium reagents, PAO solutions did not combust on contact with air. In fact, PAO solvents do not combust even after 25 seconds of exposure to a blowtorch unlike hexane solutions which ignite instantly (Figure I-36). These lithium reagent solutions in PAOs could then be used as conventional lithium reagents in conventional solvents for things like anionic polymerization.

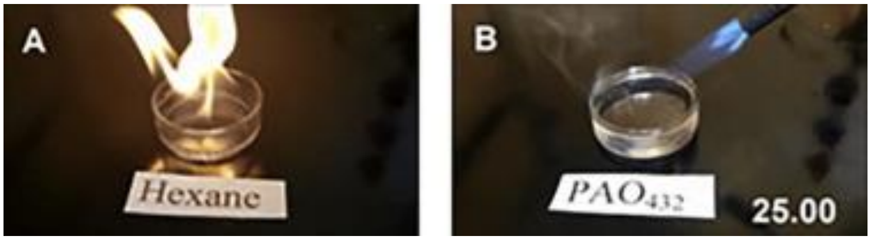

Figure I-36 PAOs are shown to be highly nonflammable in comparison to the more traditional hexane. Reprinted with permission from (58).

Another application of PAOs as a solvent phase is their use in environmental remediation of water containing trace organic components. These PAOs can also be used as recyclable, separable sequestering solvents for organic molecules from water.[60] By vigorously mixing the PAOs and contaminated aqueous phase and then centrifuging, organic molecules can be extracted into the PAOs (Figure I-37), which has great potential for removing organics such as phenols or pesticides from drinking water.

Figure I-37 PAOs extracting benzene from contaminated water. Reprinted with permission from (59).

A final recent example from Thavornpradit, Killough and Bergbreiter involved the use of PIB bound nucleophilic catalysts in PAOs. This work showed that PAOs containing these catalysts can be used to facilitate several different types of reactions as well as demonstrating several methods for the isolation of products from PAOs allowing for recycling of both the solvent and catalyst (Figure I-38).[61] For instance, these PIB bound DMAP catalysts were used for condensation reactions where a small amount of toluene was added to the PAO in order to solubilize the starting materials. After the reaction, the product could be precipitated from the reaction solution upon cooling which could be followed by centrifugation and decantation to give the isolated product as well as allowing for reuse of both the catalyst and the PAO/toluene system in further reactions. Another example from this work showed that products that do not precipitate from PAO could be isolated by simple extraction with aqueous acetonitrile, which also allowed for reuse of the PAO/catalyst system and prevented contamination of the product with PAO. This work further showed that, although cumbersome, PAO co-solvent systems could be perturbed using PEG in order to separate the products. Finally, this work demonstrated that not only can many reactions be carried out in PAOs, but the reaction rates in this recyclable solvent can be comparable to those of conventional solvents like tetrahydrofuran.

Figure I-38 Product isolation methods from PAOs. Reprinted with permission from (60).

CHAPTER II

ENTHALPICALLY DRIVEN POLYISOBUTYLENE DEPOLYMERIZATION*

Introduction

For over fifty years, there has been an intense interest in the degradation of polyisobutylene (PIB). This interest has generated hundreds of academic papers ranging from original research to reviews of the topic material.[62] These discussions have discussed and investigated numerous potential methods (mechanical, photo degradation, radiative, thermal, etc.) for PIB degradation, but all of these methods have their potential drawbacks. These methods proceed under different mechanisms that are dependent on the type of degradation. While some of these methods lead to random initiations or scissions throughout the polymer backbone, others proceed exclusively from the terminal (or starting end) of the chain or from internal alkenes.

One way to degrade PIB is to use thermal degradation. In studies by Grimbley and Lehrle[63,64] both complete and partial pyrolysis of PIB were studied at various temperatures and sample thicknesses. The pyrolysis of 10 µg of PIB_{9000} was carried out under inert atmosphere by heating a thin film of PIB to 610 °C for 30 seconds to achieve complete pyrolysis, while the incomplete pyrolysis was carried out for only 10 seconds at 400 °C. The incomplete pyrolysis of PIB_{9000} led to the formation of product fractions

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*Reprinted with permission from Watson, C. B.; Tan, D.; Bergbreiter, D. E. Enthalpy-Driven Polyisobutylene Depolymerization, *Macromolecules,* **2019**, *52*, 3042-3048.

between 4 carbon monomers and octameric oligomers (Figure II-1), although the four carbon units were the predominant product.

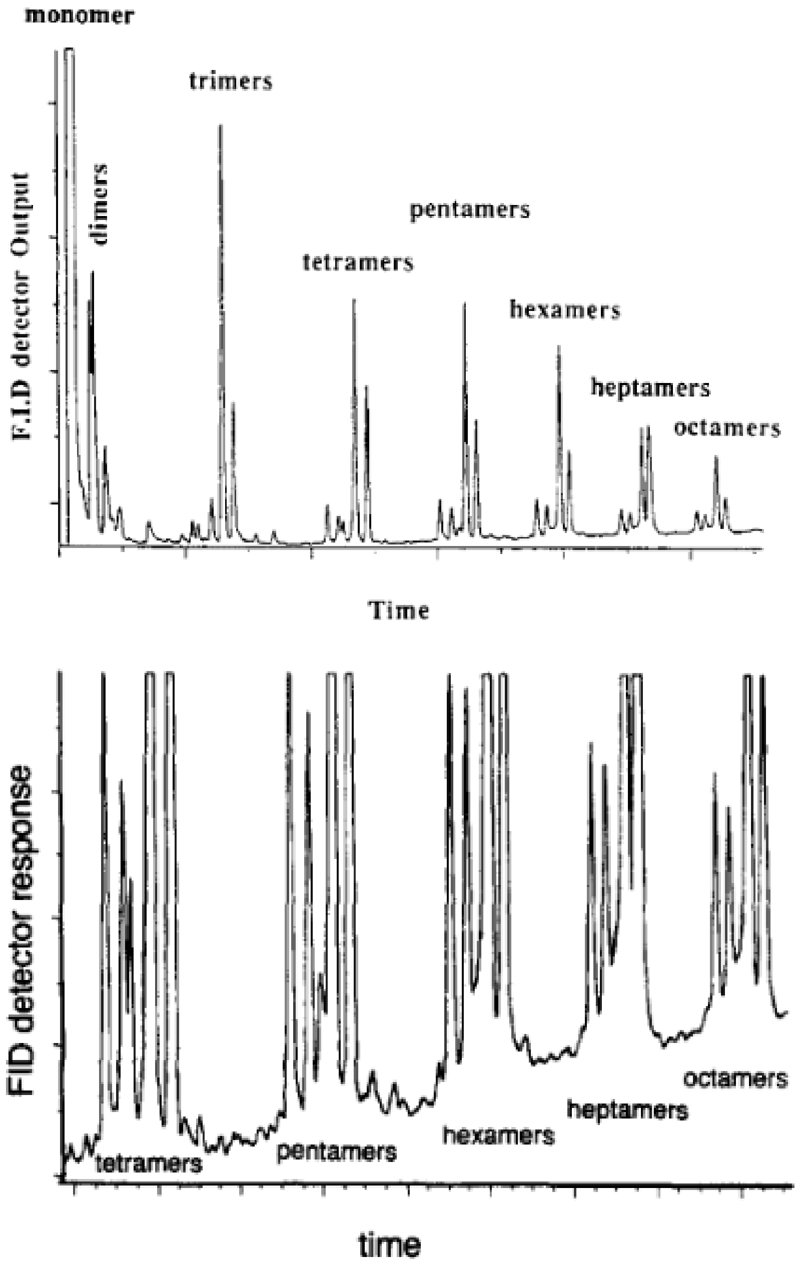


Figure II-1 (Top) Products formed after partial pyrolysis of PIB_{9000} at 400 °C for 10 seconds and (Bottom) expansion of the GPC spectra for the higher molecular weight oligomers showing multiple similar products Reprinted with permission from (63).

The proportions of these different oligomers was claimed to be consistent with a random scission mechanism of degradation leading to the formation of the relatively stable tertiary radical and the less stable primary radical. Additionally, there was a larger than statistically expected fraction of the monomer, that is accounted for by chain depropagation (or depolymerization) from the terminal radical via elimination of isobutylene to form a new radical bearing chain of the same type (tertiary or primary) that is shorter by one monomer unit (Figure II-2). However, this claim was based on a statistical analysis that was heavily criticized a decade later by Poutsma.[65] Not shown are the intramolecular abstractions, usually via 5 and 6 member transition states, which could lead to the formation of alkenes on non-terminal parts of the chain as well as further chain scission events. These processes lead to several peaks present for each molecular weight in the gas chromatogram, which are due to the formation of different unsaturated/mono/di-saturated compounds. Additionally, the carbon-carbon double bonds formed can be either internal or external, leading to a variety of potential species of similar molecular weight. While there are numerous products formed, it should be noted that the predominant product formed is the monomer of isobutylene, a result that would be useful if the goal were to reform monomer from this polymer. In other work,[66] the volatilization of the lower molecular weight oligomers that are formed has been shown to be linear with respect to time (Figure II-3).

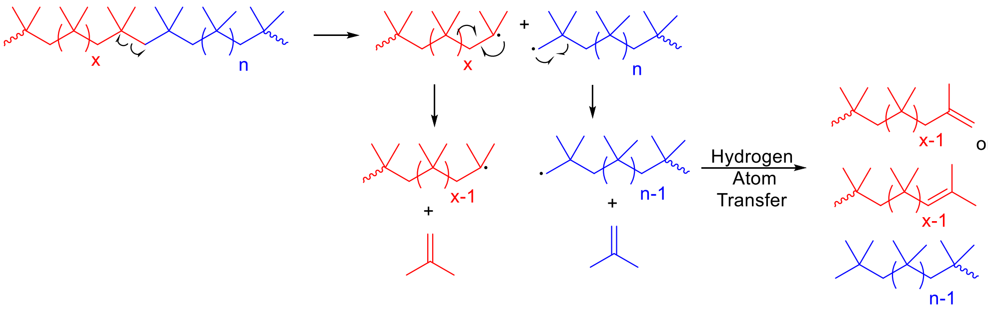


Figure II-2 Predominant mechanism of degradation proceeds to form the isobutylene equivalents. In an alternative reaction, alkenes can be formed via abstraction of the adjacent hydrogen atom (Red) or abstraction of a hydrogen atom from another molecule (Blue) can lead to alkanes

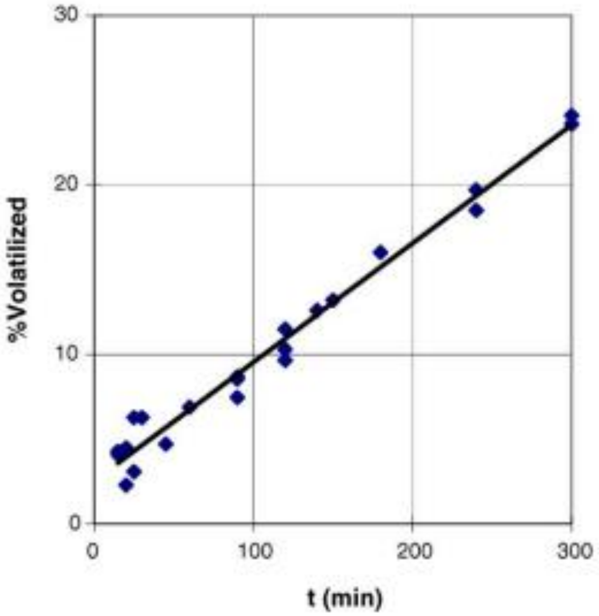


Figure II-3 At 300 °C, the volatilized material from the PIB degradations is linearly dependent on time. Reprinted with permission from (64)

This thermal degradation of PIB has the drawback of being an energy intensive process. It requires elevated temperatures for a significant degree of degradation. Despite a reported ceiling temperature of 175 ^{o}C, thermal degradations are routinely carried out at temperatures significantly above this, often at temperatures in excess of 400 °C. While this higher temperature allows the degradation to be rapid, it is a significant energy cost. Additionally, this method proceeds via a radical process as discussed above which can be very difficult to control and if you want to make a new product with the monomers you have mixtures of monomers with other products – mixtures that have to be separated. However, in contrast to other polyolefins such as polyethylene, the rate of volatilization for PIB is much faster because it disproportionates more easily due. Hemolytic chain scission produces both a primary radical and a more stabilized tertiary radical intermediate. This is in contrast to polyethylene that can only form primary radicals on chain scission (assuming no branches in the polymer chain).

Thermal degradations of PIB have also been coupled with additional reagents and catalysts in an attempt to speed this degradation. For instance, Thomas[67] used the addition of dicumyl peroxide at 140 °C in an attempt to promote degradation. Unlike the mechanism described above, the mechanism for this process was claimed to proceed predominantly via random scission of the main chain caused by attack by the cumyloxy radical on the methylene groups of the main chain. This process thus leads to attachment of the cumyloxy radicals to the degraded material via formation of an ether which prevents further degradation (Figure II-4). No evidence was found for depolymerization of the main chain at this lowered temperature. Evidence given for this mechanism was the lack of acetophenone and cumyl alcohol formed. This would be consistent with minimal hydrogen abstraction, meaning the hydrogen abstraction mechanism is unlikely. They thus proposed the mechanism below.

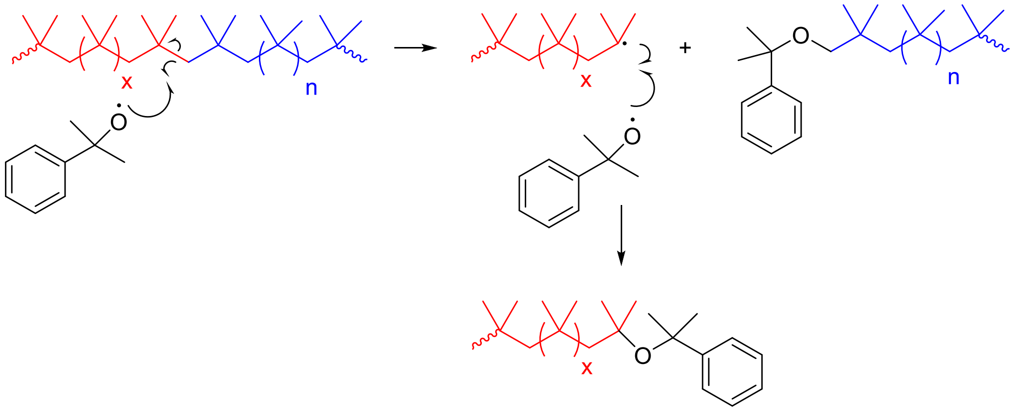


Figure II-4 Random chain scission by cumyloxy radical to give the stable ether, preventing depolymerization.

Photo-oxidative degradation of PIB has also been attempted at 30, 60, and 90 °C by Gardette and coworkers.[68] Their study used thin films of PIB under that were irradiated in air by mercury lamps with the radiation below 300 nm filtered out. These conditions were meant to cause accelerated photo aging under conditions replicating natural weathering. From the IR spectra of their studies (Figure II-5), it is shown that significant amounts of the PIB ketone (1730 cm^{-1}), carboxylic acid (1702 cm^{-1}), and β-lactone (1832 cm^{-1}) are all formed over time. Alkene and alcohol products were also seen. The relative amounts of these products varied with temperature. They attributed the difference in the relative amounts of various products formed at different temperatures to competing mechanisms between a photo-oxidation at lower temperatures and a thermal oxidation at higher temperatures. However, hydroperoxides are the most important intermediate from radical auto-oxidation of the polymer. The rate of the formation of this intermediate is dependent on both the intensity of the light as well as the temperature, increasing as both increase. The radicals generated from these peroxides can then give oxidations to alcohols, acids, esters, ketones, and lactones as well as alkenes.

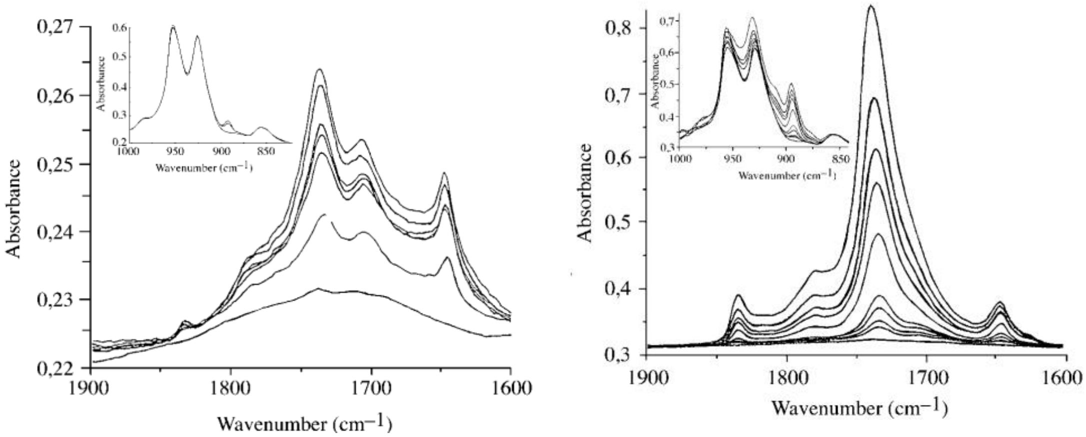


Figure II-5 (Left set of spectra) The IR spectra changes over 2300 hours for the photo-oxidation of PIB under a mercury lamp and air at 35 °C. (Right set of spectra) The IR spectra rising over 350 hours for the photo-oxidation products of PIB under a mercury lamp and air at 90 °C. Reprinted with permission from (67)

Lehrle and Pattenden also looked at the degradation of PIB in toluene, methylcylcohexane, and carbon tetrachloride when being subjected to gamma radiation from a cobalt source (Figure II-6).[69] Their results show that the gamma radiation leads to chain scission and causing reduction in molecular weight, but the degree of this scission occurring is dependent on both the solvent and the dosage of gamma radiation used. This further led them to conclude that the PIB polymer itself is not the initial target of the radiation. Instead, the solvent itself undergoes scission to give radicals that then interact with the polymer chains leading to random scission of the PIB. The result is predominantly random scission, and as such significant amounts of the monomer formation are not observed. This initial solvent interaction causes the more susceptible carbon tetrachloride solvent to degrade the polymers more with the same amount of radiation. However, the importance of this solvent effect was likely due to the relatively low concentration (0.01g / mL) of PIB. Pomery and coworkers[70] showed that this solvent is unnecessary by irradiating 4 samples at 125 °C PIB virgin could be degraded without solvent (Figure II-7). They further showed that in the absence of solvent, the radiation still leads to chains scission by a radical mechanism.

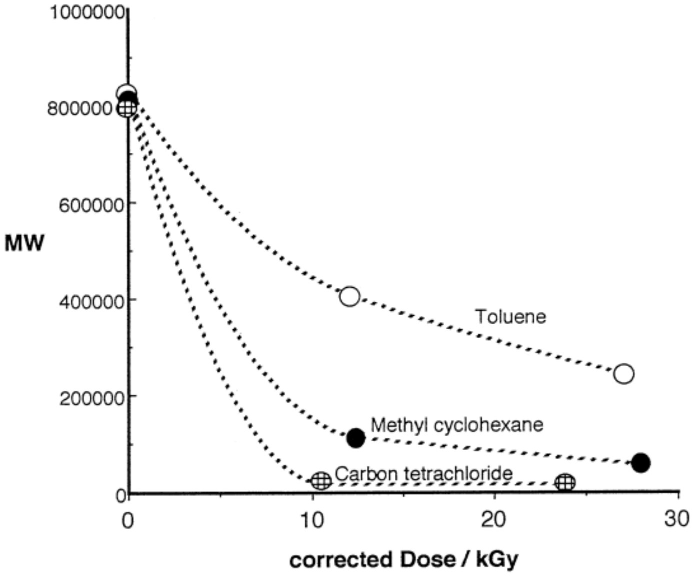


Figure II-6 Decrease in molecular weight of the PIB chains as function of gamma dosage in three different solvents. Reprinted with permission from (68).

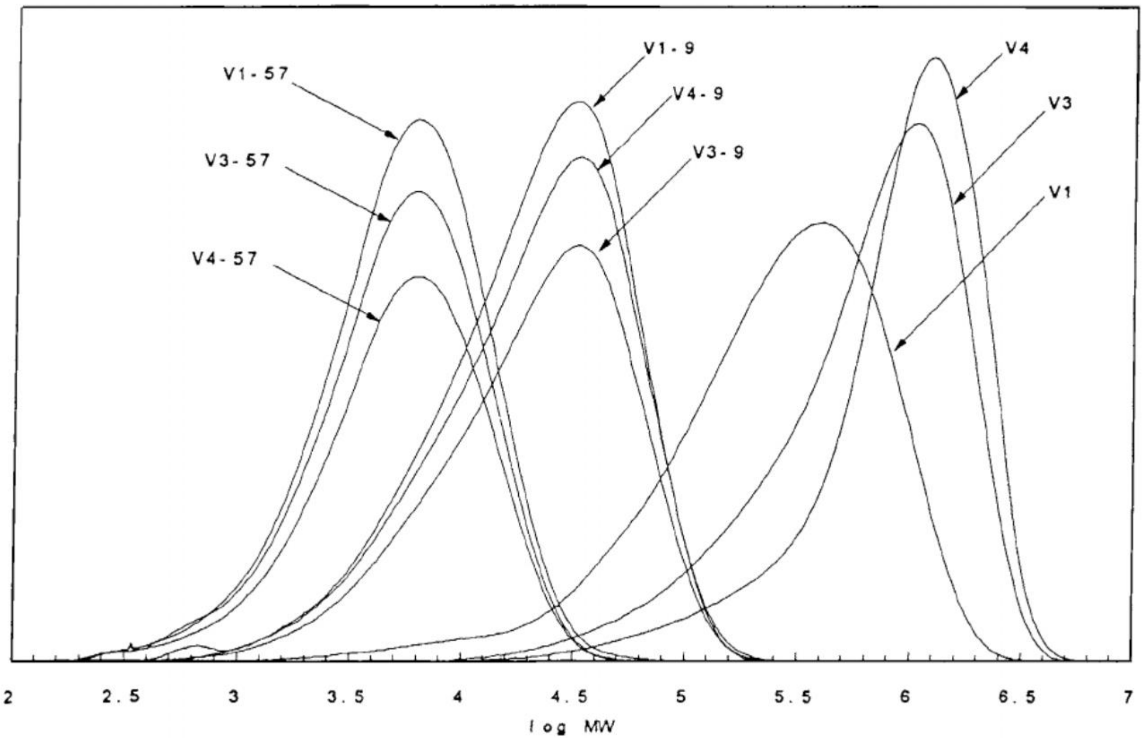


Figure II-7 The log of the molecular weight for 3 virgin samples (V1, V2, V3) that had been irradiated with 0, 9, and 57 kGy total dose. Each peak is labeled by the sample and then the irradiation amount is listed after the dot. Reprinted with permission from (69).

PIB can also be degraded under mechanical conditions. An example from Jhon and coworkers uses PIB in kerosene in a rotating disk apparatus to see the effect of turbulent flow on the molecular weight of the polymer.[71] In this study, the high shear and elongational strain cause degradation by scissions in the polymer back bone leading to radical formation. These scissions tend to be random and thus lead to rapid and chain shortening (Figure II-8). They found that at 1800 rotations per minute, the chains rapidly degraded and the polydispersity increased dramatically from 1.5 to 4.5 as expected for random scission.

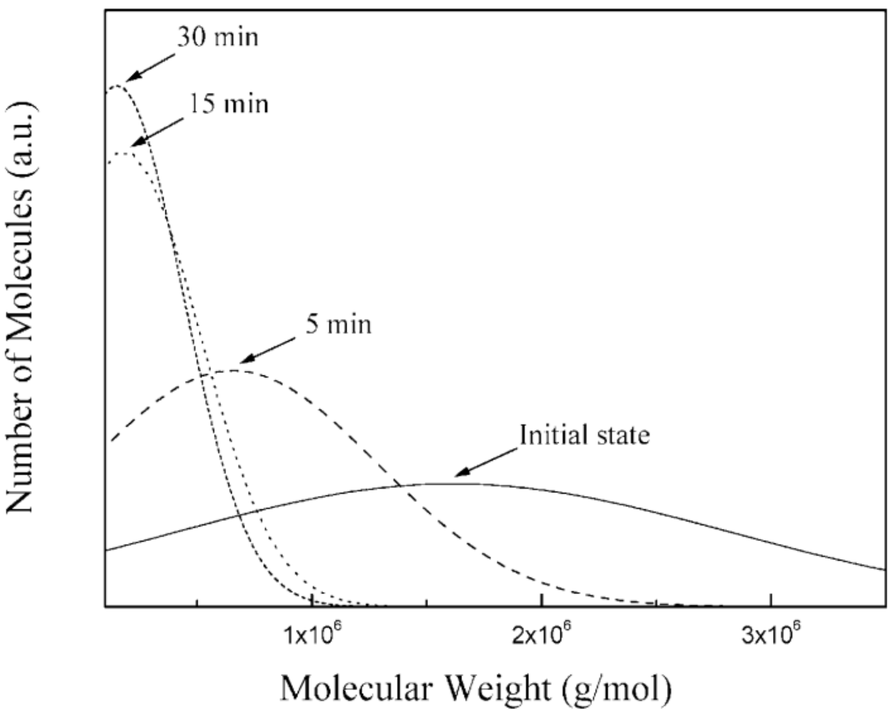


Figure II-8 Change in molecular weight and total number of chains of PIB over time during turbulent flow. Reprinted with permission from (70).

While all of the above methods do lead to degradation, the issues with product distribution, incomplete degradation and energy intensity are problematic. Cationic degradation is an alternative process that can be used that can lead to increased formation of the isobutylene product.

Cationic degradation of polyisobutylene can be accomplished at elevated temperatures, and has been discussed by Prochukhan and coworkers.[72] At 360 °C they showed that aluminum catalysts ($NaAlCl_4$ and $NaEtAlCl_3$) degrade the PIB by formation of *tert*-butyl carbocations by protonation at the terminal alkene bond. Once these carbocations are formed, they can depolymerize to give isobutylene. They showed that the rate of isobutylene generation is dependent on both the type of catalyst and on catalyst concentration. This sort of cationic degradation yields up to 90% of the isobutylene monomer, a significant difference versus the un-catalyzed thermal processes. By reducing the temperature to 180 °C and the use of a different aluminum catalyst ($C_4H_9[EtAlCl_3]$) more than 98% of the PIB chains could be converted into the monomer units via an end protonation and depolymerization.

Cationic degradation at ambient or even sub ambient temperatures has also been attempted, although with less success. One study from Kennedy's group[73] attempted to use ethyl aluminum dichloride at -10 °C to degrade PIB in alkane solvents. This however led to no observed change in the molecular weight of the polymer. A more promising example by Storey and coworkers[74] showed that the use of $TiCl_4$, an alkoxy benzene quenching solvent, and a protic catalyst could lead to scission at internal double bounds of a PIB chain (Figure II-9). This mechanism proceeds via protonation of the double bond to give the relatively stable *tert*-butyl cation, followed by scission of the chain to give another *tert*-butyl cation and an alkene. The alkene can be further protonated and then attacked to give the PIB chloride followed by attack by the solvent to give the aromatic alkoxy end group.

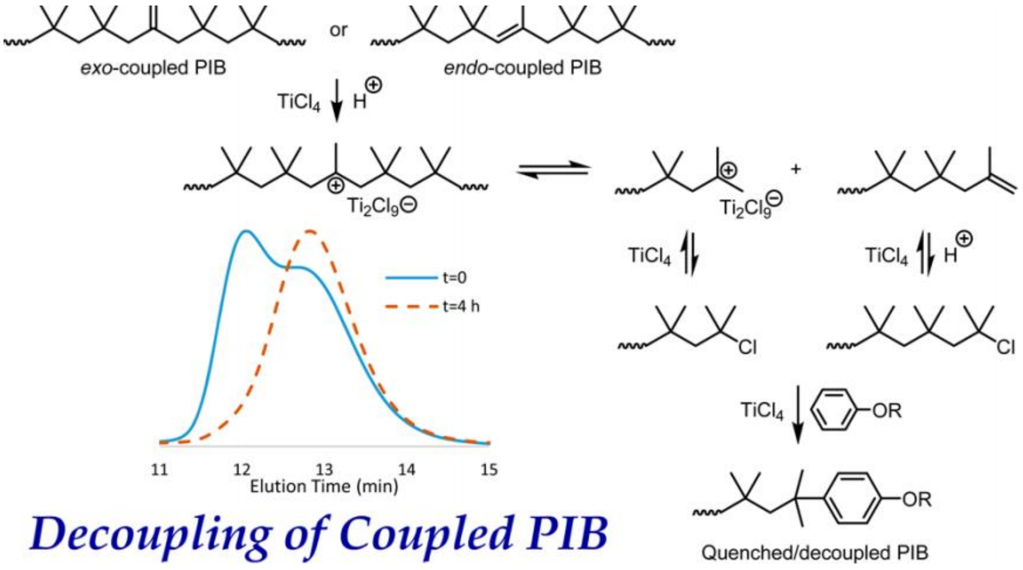


Figure II-9 Decoupling of coupled PIB by hetero lytic cleavage. GPC spectra shown for expected decrease in molecular weight without further depolymerization. Reprinted with permission from (73).

As discussed above, cationic degradation has historically also required either elevated temperature, or simply led to incomplete degradation. In the studies described in this chapter, we showed that complete PIB degradation can be seen even at low temperatures. Specifically, my studies showed that using triflic acid and an arene solvent lead to conditions where isobutylene units are captured by solvent as they form. In principle, the excess solvent thus drives the reaction to completion by Le Chatelier’s Principle. A second factor is that the bond energy difference between a C-C bond in the polymer and in an alkylated arene is different. This makes degradation thermodynamically favorable in enthalpic terms. This depolymerization thus differs from other processes where the entropy of polymer degradation is the driving force for polymer degradation.

Our initial interest in this chemistry arose from several synthetic observations in our lab that are summarized in Figure II-10 below. In attempting to attach arenes to PIB via Friedel-Crafts chemistry, I and others found that we could not use alkene terminated PIB oligomers as electrophiles in an acid-catalyzed electrophilic aromatic substitution if we used simple arenes. This reaction failed with a stoichiometric or a slight excess of toluene or benzene with H_2SO_4 as a catalyst in dichloromethane. It also failed to form the desired product with a stronger acid –triflic acid (CF_3SO_3H). Others[75] showed that this reaction also failed at elevated temperature due to the modest thermal stability of PIB alluded to above. When more forcing conditions were used, such as heating with sulfuric acid, small amounts of *tert*-butyl aromatics were formed, suggesting that some isobutylene was being generated. Though in those reactions alkene substituted PIB was still the major product. Even adding the arene in vast excess as a solvent led to no benzene or toluene terminated PIB oligomer. Essentially, a vinyl-terminated PIB oligomer was entirely immune to attack by weakly activated arene substrates. This is in contrast to work where similar alkene terminated PIB oligomers are allowed to react with electron rich arenes such as phenol, anisole, or anilines. These activated arenes all react with PIB alkenes to give arene terminated oligomers via electrophilic aromatic substitution.[14] While benzene and toluene are unsuitable as substrates for electrophilic aromatic substitution of an alkene-terminated PIB, it is known that isobutylene itself, in the presence of a Brønsted acid is a suitable electrophile for formation of *tert*-butylbenzene or 4-*tert*-butyltoluene.

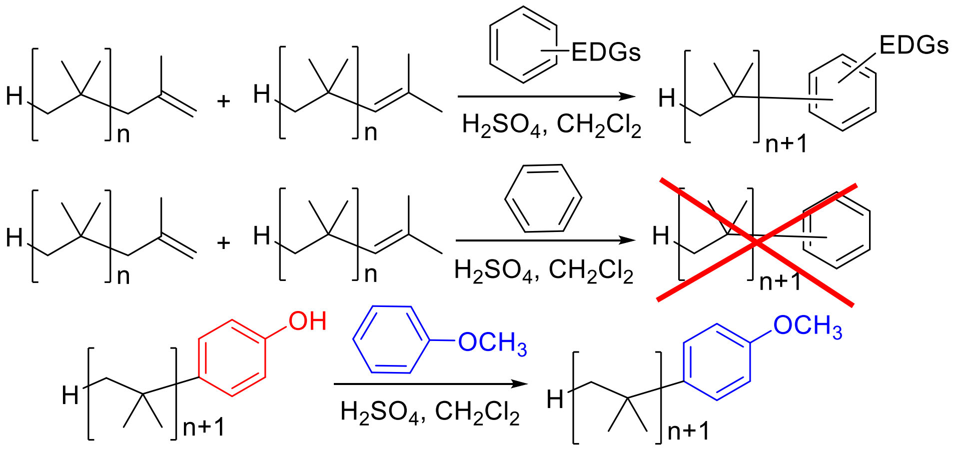


Figure II-10 Summary of previous observations within our group.

We reasoned that one reason the reactions in Figure II-10 did not work is because of the well-known de-*tert*-butylation reaction of *tert*-butylarenes. This reaction occurs because *tert*-butyl groups on arenes can undergo ipso-substitution with protons from a Brønsted acid. This reaction produces isobutylene as a product and has been used in small molecule chemistry where the *tert*-butyl group serves as a “protecting group” for a proton. That same reaction has been used in polymer chemistry too, where rigid rod arene-containing polymers are solubilized with *tert*-butyl groups that are eventually removed to form a final polymer product with high T_g values. In the case of PIB chemistry, these same processes can occur. For example, it has been noted that the electron rich arene end groups attached to PIB can be removed by treatment with acid. For instance, in the presence of a strong acid, the phenol end group could be exchanged for anisole when phenol-terminated PIB was allowed to react with acid in anisole as a solvent by the mechanism in Figure II-11. These observations led us to believe that PIB with arene groups could be in equilibrium with a cation terminated PIB. If this were true, under the correct conditions, PIB could be degraded if the PIB cation exists in equilibrium with some small amount of transient isobutylene, and if that isobutylene could be capture irreversibly, this could in effect drive a depolymerization forward.

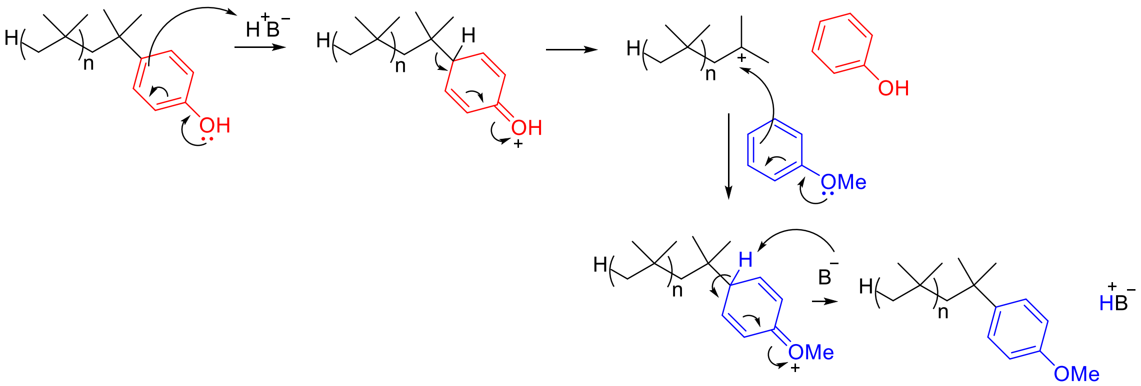


Figure II-11 Mechanism for acid catalyzed exchange of phenol end group for anisole end group

Based on these ideas, we thought we could design systems that remedy two of the historic problems with degradation of polyolefins like PIB. First, we suggest that it should be possible to design systems that will allow for ambient (and even sub ambient) temperature degradation. Second, we show that these systems will also allow for complete depolymerization of the initial polymer rather than either partial degradation or merely scission of the polymer chain. This depolymerization process in the presence of arene solvents had been previously shown to only form *tert*-butyl arenes in the presence of PIB at elevated temperatures. The work described below shows that pairing arene solvents with triflic acid allows for complete degradation of a PIB polymer chain via an end group driven depolymerization even at sub-ambient conditions in minutes.

Results and Discussion

In our initial studies, a large excess of the acid being tested (1 mL) was added to a solution of 1 g of alkene terminated PIB in 6 mL of benzene or toluene. We used NMR spectroscopy to observe the formation of the ^{1}H proton singlet at 1.3 ppm that is due to the methyl groups on the generated tert-butyl arene. We followed the changes in the intensity of this peak relative to the intensity of the CH_2 singlet at 1.4 ppm on the PIB polymer backbone as a function of time. These initial conditions were used to determine which acid, if any, could be used to facilitate PIB depolymerization. A variety of inorganic and organic acids were tested for this initial screening in benzene and toluene with terminal PIB_{1000} alkene. Concentrated sulfuric acid, hydrochloric acid, hydrobromic acid, trifluoroacetic acid, and methanesulfonic acids were all examined. However, minimal formation of the butylated arene was detected after 24 hours. In contrast, we observed that triflic acid led to observable amounts of *tert*-butyl arene formation. Further, we found that the 11 equivalents of triflic acid used in these initial studies were not required. One equivalent of the acid achieved nearly complete depolymerization in benzene or toluene.

Our initial studies used a 24-hour reaction time. However, this depolymerization process appears to be an extremely rapid process. Indeed subsequent studies showed that near total depolymerization can be achieved within the five minutes of reaction time. These experiments will be discussed below along with the gel permeation chromatography (GPC) (or size exclusion chromatography (SEC)) data. In addition I observed that under some conditions, another rearrangement reaction does proceed after depolymerization and I provide a brief discussion of that chemistry too in the discussion below.

To explore this depolymerization process, we first screened arene solvents with electron withdrawing or electron donating substituents in PIB depolymerization. These experiments involved ^{1}H NMR studies like those above and were carried out for 24 hours with 11 equivalents of triflic acid at room temperature (Figure II-12).While the studies like those discussed above showed that PIB readily degraded in both toluene and benzene, PIB degradation occurred but to a much lower extent in chlorobenzene. Presumably this is due to the reduced ability of the electron poor chlorobenzene to act as a nucleophile in electrophilic aromatic substitution. This results in the depolymerization process being significantly slowed. In contrast, essentially no depolymerization of the PIB occurred in anisole. We ascribe this to a solvent leveling effect. While we used triflic acid in all these experiments, triflic acid is acidic enough so that it likely forms a protonated arene. Thus, in anisole as the solvent, the likely acid present is in fact the protonated ether. This is presumably not acidic enough to facilitate depolymerization.

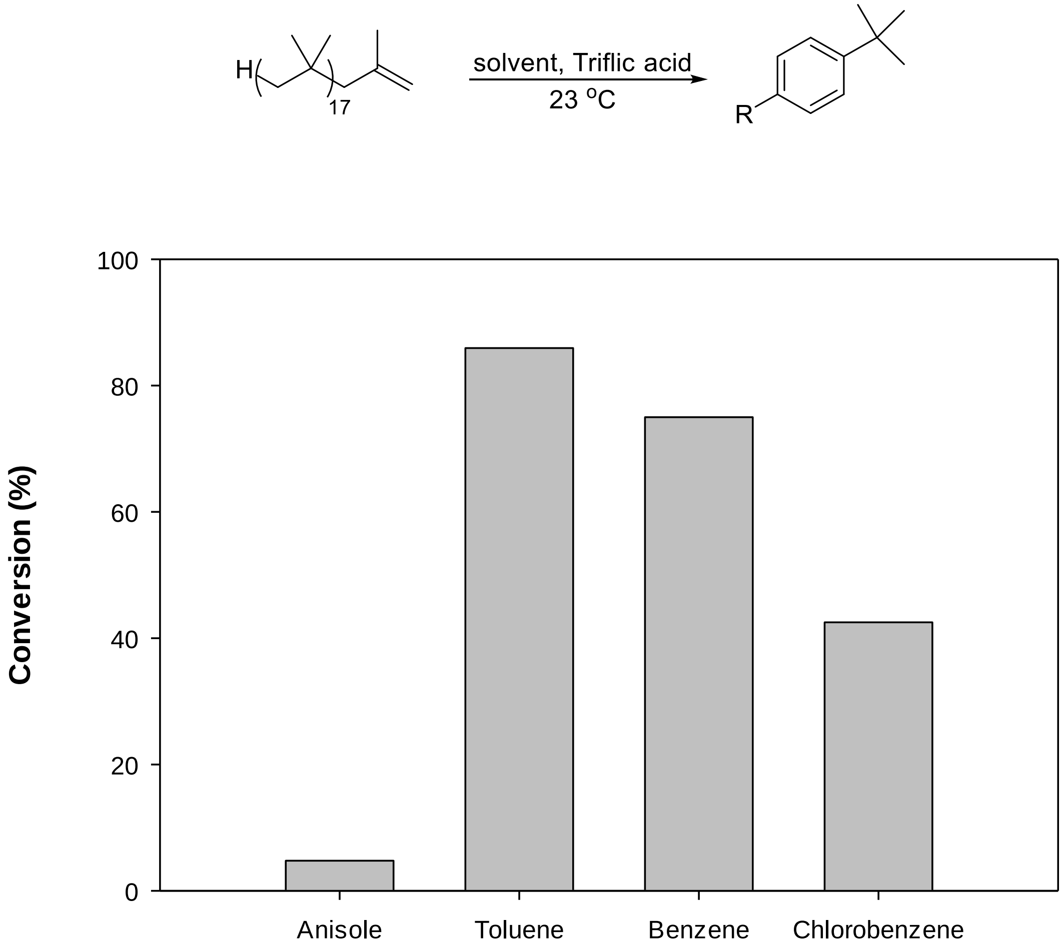


Figure II-12 The degree of PIB_{1000} alkene degradation calculated by comparing the ratio of singlet of the generated *tert*-butyl arene relative to the remaining PIB methylene peak using ^{1}H NMR spectroscopy.

All of the experiments above were carried out with alkene terminated PIB. We thus next tested other functionalized PIB with numerous end groups (Figure II-13) in toluene with triflic acid at room temperature to test the effect of the end group on the depolymerization process. The syntheses for these functionalized PIB derivatives were based on published procedures.[76] The PIB alcohol **2** was made from the alkene terminated PIB **1**. This involved a hydroboration, oxidation reaction. This alcohol was then converted using an Appel reaction into the PIB iodide **3** by triphenyl phosphine, imidazole and iodine. The alkene **1** was also used as a precursor for the ketone. This ketone **4** was formed from the alkene terminated PIB via ozonolysis. The PIB methyl ketone **4** so formed can subsequently be transformed into the PIB carboxylic acid **5** via the iodoform reaction. The PIB anisole **6** was made following a known procedure by dissolving the PIB alkene **1** into anisole and stirring overnight with sulfuric acid. The phenol **7** can be made similarly but with addition of dichloromethane in order to dissolve the solid phenol.

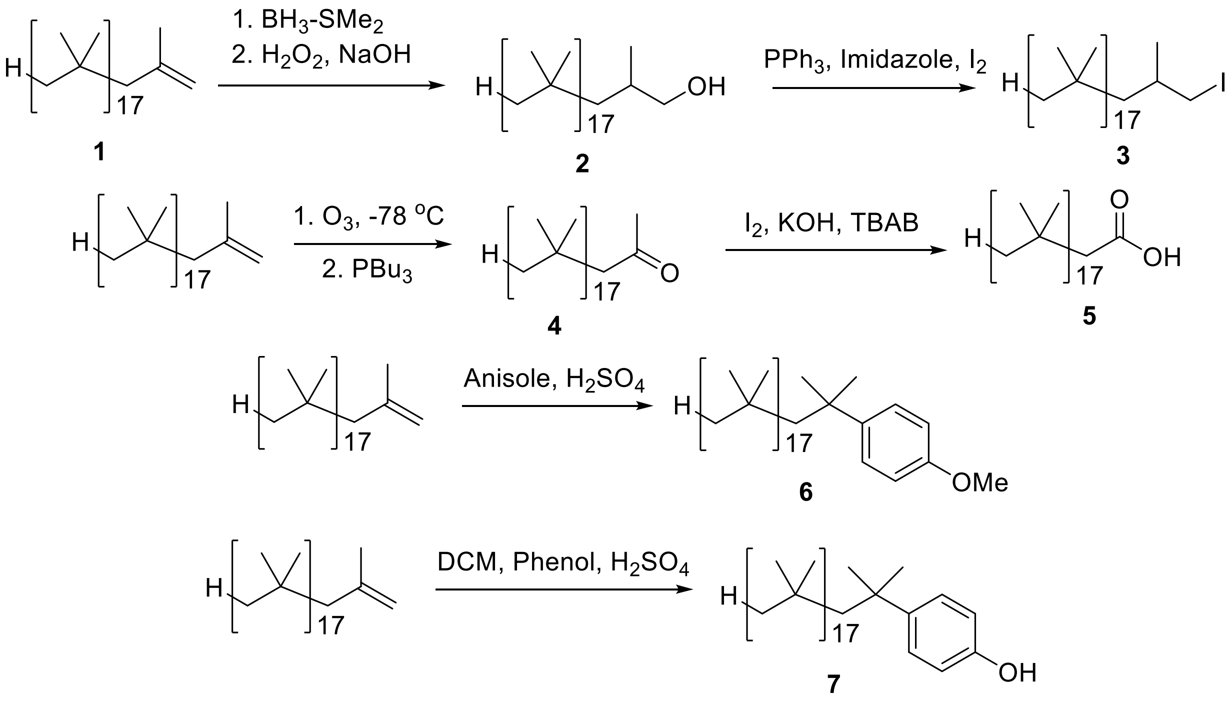


Figure II-13 Synthetic routes to different end functionalized PIB_{1000} oligomers.

Toluene was chosen as the depolymerization solvent in this experiment both because it is a good solvent for this depolymerization, and it simplifies the quantification of the process. This is because toluene almost exclusively forms a single product (4-*tert*-butyltoluene), while the benzene can form both the mono *tert*-butylated product (*tert*-butylbenzene) and the di *tert*-butylated product (1,4-di-*tert*-butylbenzene).

The effect of the end groups on the degree of depolymerization of the polymer in toluene with two equivalents of triflic acid and 6 mL of solvent per gram of PIB was then analyzed via ^{1}H NMR spectroscopy. It was found (Figure II-14) that any end group which could form a *tert*-butyl carbocation could lead to the depolymerization of the polymer via formation of an isobutylene unit and a cationic oligomer chain that was one unit shorter. However, end groups that were incapable of forming this *tert*-butyl carbocation showed effectively no depolymerization of the PIB chain, and no formation of the tert-butyltoluene. For instance, an iodide-terminated PIB was inert under our depolymerization conditions, as were the ketone and the carboxylic acid. While the PIB alcohol could eliminate to form the alkene and thus degrade, with only two equivalents of acid used, depolymerization was not seen. We ascribe this to the fact that the water formed by this elimination would consume one equivalent of the triflic acid to form H_3O^+ and $CF_3SO_3^-$. While one equivalent of triflic acid should still be present, it is possible that the second equivalent of triflic acid is stabilized by H_3O^+ and $CF_3SO_3^-$. It should be additionally noted that in the presence of large excess of acid (11 equivalents), the alcohol did undergo depolymerization. Both of the arene terminated PIB substrates gave large degrees of depolymerization, likely due to ipso substitution of the arene end group discussed earlier. The incomplete depolymerization of these PIB arenes is likely due to the phenol and anisole products of this ipso substitution undergoing protonation, consuming one equivalent of the acid. The alkene as previously discussed undergoes a high degree of depolymerization. The incomplete amount of depolymerization for alkene terminated PIB shown in Figure II-14 is likely due to the 5-10% of the unfunctionalized PIB alkane that is also present in these samples.

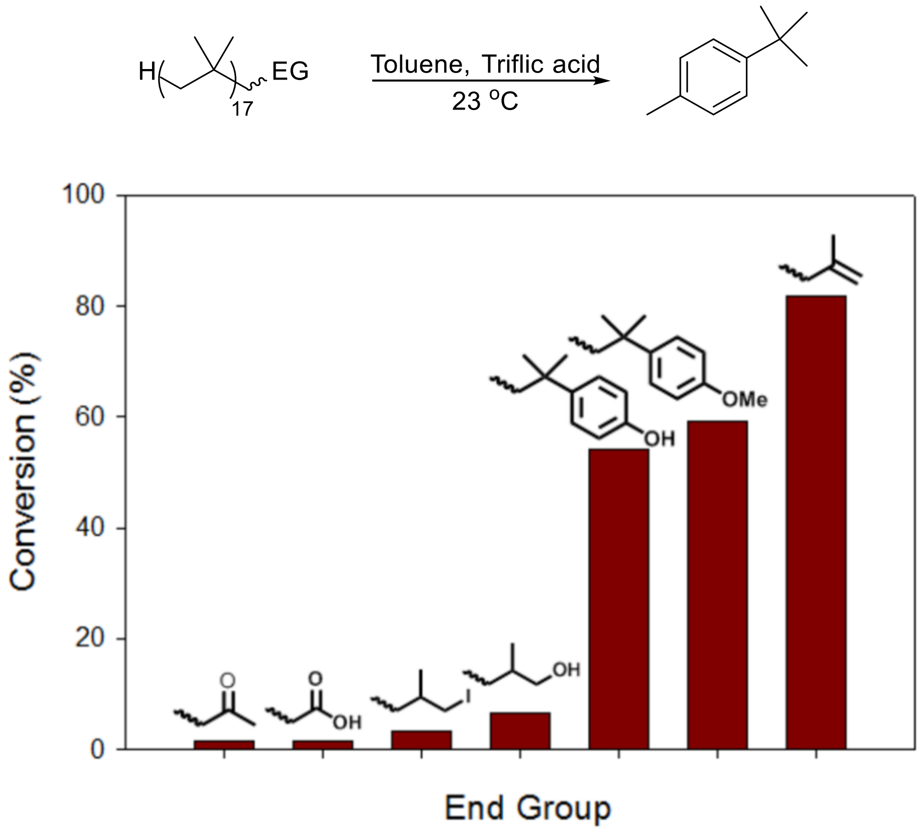
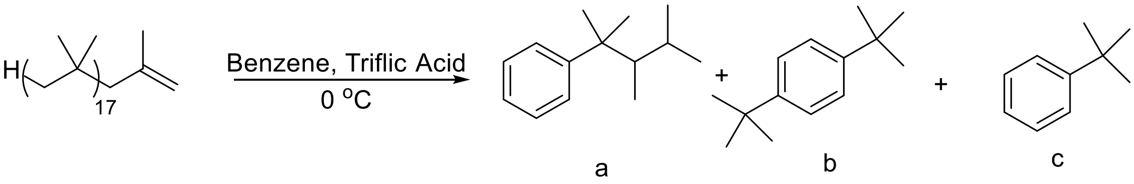


Figure II-14 Degree of PIB_{1000} degradation for different end groups calculated by comparing the ratio of singlet of the generated *tert*-butyltoluene relative to the remaining PIB methylene peak using NMR Spectroscopy

While these initial studies were insightful and provide us with useful information about this novel strategy for depolymerization, we decided that further studies using gel permeation chromatography (GPC) (or size exclusion chromatography (SEC)) would be desirable. These studies were undertaken in order to show the degree of depolymerization as well as the size of the molecules being formed. For instance, our ^{1}H NMR spectroscopic analysis cannot differentiate between small chain fragments attaching to the arene, and a single tert-butyl attachment. In contrast, a GPC analysis can differentiate between the starting oligomers and mono- and disubstituted arenes. These GPC studies used a column designed for separating short chain oligomers using tetrahydrofuran as a solvent.

We first retested the triflic acid using one and two equivalents in order to study the rate and degree of depolymerization at lower temperature (0 °C). We took timed samples spanning the first hour in order to get a crude estimate of the reaction rate. In this study, 1 mL aliquots were taken at the stated time and any triflic acid was removed before analysis by passing 1 mL of the reaction mixture through a plug of silica gel. The sample was then concentrated under reduced pressure to remove excess benzene. When the depolymerization was carried out with one equivalent of acid (Figure II-15), we found that the reaction is essentially complete within the first minute. The GPC spectra showed three products formed. Product (c) is the expected *tert*-butylbenzene product. The identity of which was confirmed by both mass spectroscopy and NMR spectroscopy. Product (b) is 1,4-di-*tert*-butylbenzene. Its identity too was also confirmed by mass spectroscopy and NMR spectroscopy. We were initially surprised by the fact that the amount of the 1,4-di-*tert*-butylbenzene product (b) is much larger than that of the mono-*tert*-butyl product (c), based on the size of the peaks in the GPC chromatogram. However other studies suggest that is likely do to some loss of the *tert*-butyl species when the benzene is removed. It may also be in part because parts of the benzene solution begin to freeze at 0 ^{o}C which may cause an artificially low concentration of available benzene to attack the generated carbocations. It should be noted however, that the peaks in GPC spectra are qualitative not quantitative, as the response intensity of a peak or its integration is dependent on more than the concentration of the material in solution.

The fact that three peaks formed was initially confusing. Our first hypothesis was that we had formed some of the tri-substituted arene. This could involve formation of either 1,2,4-tri-*tert*-butyl or 1,3,5-tri-*tert*-butylbenzene. While the molecular ion in the mass spectrum of product (a) indicated that (a) had the same molecular weight as the expected 1,4-di-*tert*-butyl product (b), its ^{1}H NMR spectrum was markedly different. In the ^{1}H NMR this product was more complex. It showed a singlet around the expected value of 1.3 ppm but also had complex peaks between 1.3 and 1.4 ppm. Additionally it had peaks between 0.7 and 0.9 ppm. The ratio of aromatic protons to aliphatic protons was also consistent with the presence of a mono-substituted arene. This peak was subsequently identified as the 1,1,2,3-tetramethybutylbenzene by ^{1}H spectroscopy.



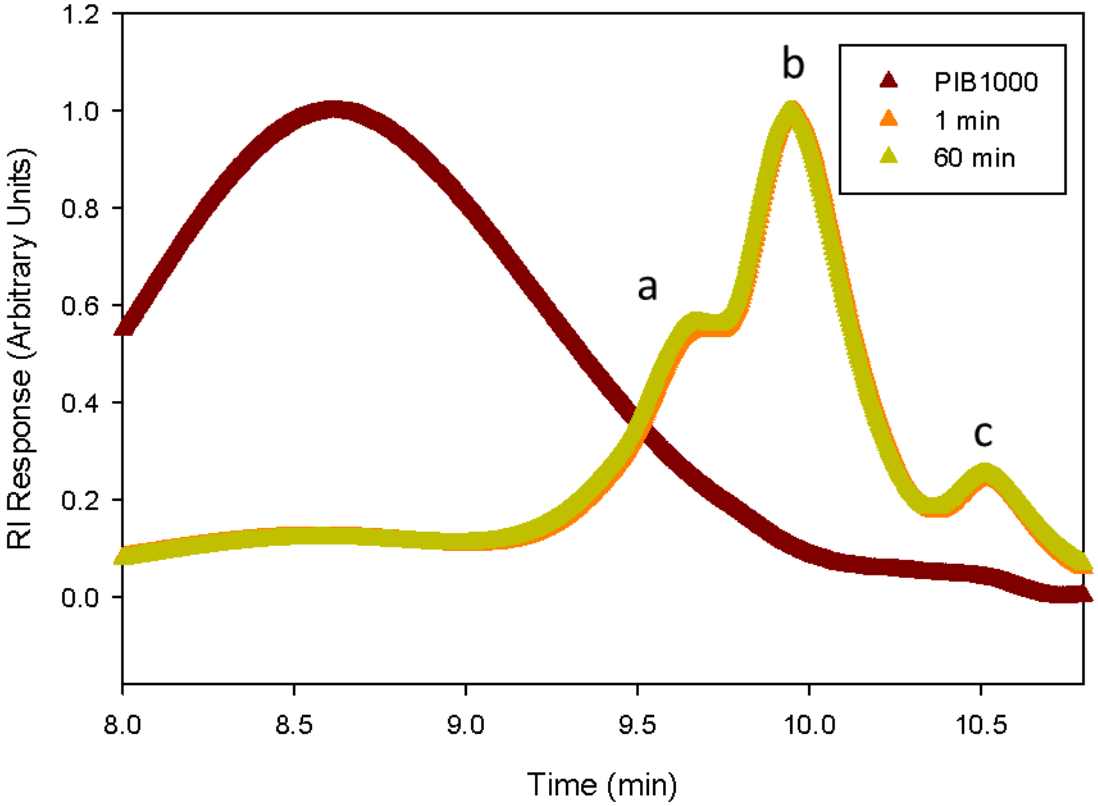


Figure II-15 GPC spectrum of products for 1 g of PIB$_{1000}$ alkene depolymerization over time with 1 equivalent of triflic acid in 6 mL of benzene at 0 °C.

The formation of 1,1,2,3-tetramethylbutylbenzene presumably proceeds via formation of a corner protonated cyclopropane ring (Figure II-16) of the penultimate dimeric carbocation formed after depolymerization of the PIB chain. This process presumably could occur at any point during the depolymerization. However, any similar rearranged carbocation will form an alkylated benzene that can undergo ipso substitution, reforming this cation that could reform some of the secondary carbocation that could lose another isobutylene group. Alternatively, this rearrangement is suppressed during the rest of the chain depolymerization due to additional steric hindrance of the larger substituents that would be present on the ring when the PIB is larger than the dimer.

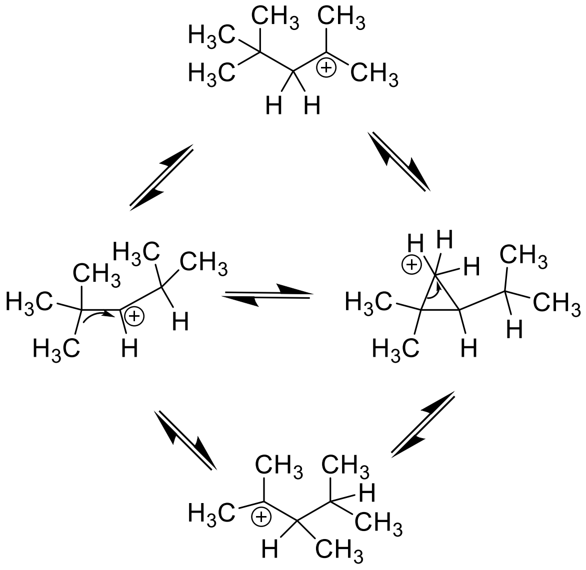
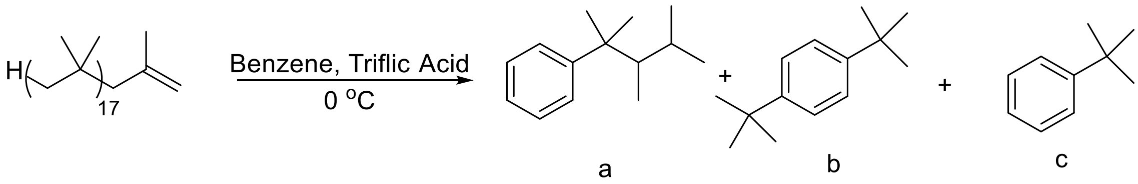


Figure II-16 Rearrangements that could convert the tertiary 2,4,4-trimethyl carbocation 1 **into a structurally isomeric 2,3,4-trimethylpentyl tertiary carbocation** 4 **that could form the minor product 1,1,2,3-tetramethylbutylbenzene**

When two equivalents of acid (Figure II-17) were used, the PIB is also completely absent after 5 minutes. However, the composition of these samples appeared to change over time. Interestingly, in the sample with excess acid, we see the same initial response of the di-tert-butyl product and then as the reaction proceeds, the response of the mono-tert-butyl product increases relative to that of the di-tert-butyl product. This is in agreement with known chemistry that in the presence of excess acid, these arenes can undergo ipso substitution that leads to loss of a tert-butyl group as a cation. The tert-butyl cation can then undergo attack by an excess benzene equivalent. This leads to conversion of 1,4-di-*tert*-butylbenzene to *tert*-butylbenzene by mass action, as there is significant excess of the solvent benzene to drive this reaction.



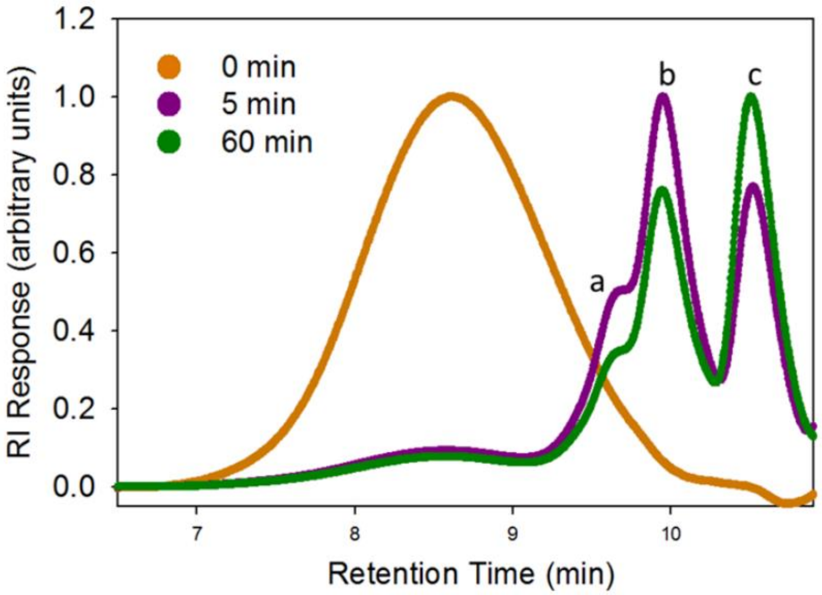


Figure II-17 GPC spectrum of products for 1 g of PIB_{1000} alkene depolymerization over time with 2 equivalent of triflic acid in 6 mL of benzene at 0 °C.

We then reexamined the effect of different end groups for PIB for this depolymerization using GPC. Based on our previous ^{1}H NMR spectroscopic studies, our hypothesis was that end groups that could not readily generate a carbocation end group in the PIB oligomer would lead to little or no PIB oligomer depolymerization and thus lead to minimal formation of the *tert*-butylarene. In order to attempt to force the depolymerization of these functionalized PIB_{1000} oligomers, 11 equivalents of the acid were used. These studies confirmed that PIB_{1000} oligomers with iodide, carboxylic acid, and ketone end groups underwent minimal depolymerization even with 11 equivalents of acid in toluene (solid) or benzene (dotted) at ambient temperature (Figure II-18). Even with this large excess of acid, these groups were still not degraded completely. In contrast, phenol, anisole, alkene and alcohol groups were all degraded completely in the presence of large excess of acid in either benzene (dotted lines in Figure II-18) or toluene (solid lines in Figure II-18) at ambient temperature.

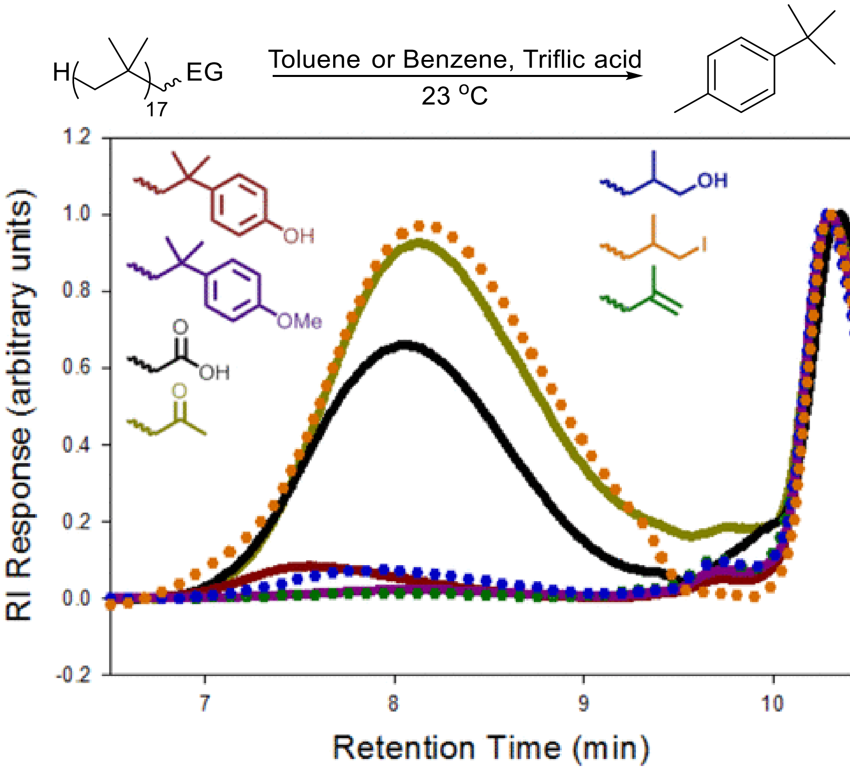


Figure II-18 GPC trace of PIB_{1000} with different end groups in the presence of benzene (dotted) or toluene (solid) and 11 equivalents of triflic acid at room temperature after 20 hours.

The PIB-iodide does not undergo depolymerization due to its lack of a protonatable group. The ketone and carboxylic acid both can be protonated by triflic acid (Figure II-19), but the reaction likely stops for the ketone as it is not a good enough leaving group to eliminate. The carboxylic acid likely protonates. However, it likely would protonate on the carbonyl oxygen. Even if some protonation occurred at the –OH group and if water elimination occurred, the cationic product that would form would be the relatively stable acylium cation that is unlikely to eliminate further. The initial alcohol undoubtedly protonates, which can then eliminate to the alkene. The water is then protonated which accounts for one equivalent of the acid. While with only two equivalents, the reaction then stops, perhaps because the second equivalent is consumed by some trace water in the benzene, or perhaps because the H_3O^+ and $CF_3SO_3^-$ makes the remaining CF_3SO_3H less acidic. In any case, with this large excess of acid, the depolymerization does proceed to completion. As expected the PIB-phenol, anisole, and alkene all depolymerize under these conditions. Because of the large excess of acid as well as the increased reaction time (20 hours), the only major products generated here are the mono-*tert*-butyl species, because any of the disubstituted species would have been converted to the mono-substituted species as discussed above.

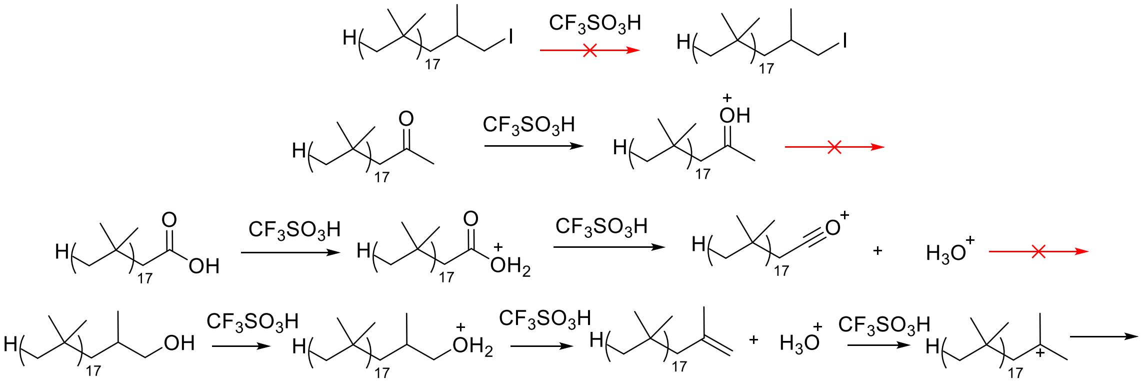


Figure II-19 Possible intermediates of functionalized PIB in presence of triflic acid.

Finally, to confirm that this process was an end group driven process as it appeared to be, we then made an unfunctionalized PIB_{1000} by hydrogenation of PIB-alkene using palladium on activated carbon. Under our conditions of 11 equivalents of acid and room temperature in benzene or toluene, this unfunctionalized PIB underwent no depolymerization, confirming that this is an end group driven process.

We then proceeded to reanalyze the degradation of PIB_{1000} alkene with 2 equivalents of acid in the stated solvent at room temperature, which had previously been done using ^1H NMR spectroscopy via GPC (Figure II-20). What we found was that the ^1H NMR study was a reasonably good approximation of the degree of depolymerization. The depolymerization does appear to still be highly solvent dependent. This is again likely due to solvent leveling in the case of anisole. The anisole does appear to degrade a small amount of the PIB to the tert-butyl anisole. Perhaps after a much longer reaction time, this anisole could fully degrade the polymer, but this would take an impractically long period of time. The toluene and benzene both show complete depolymerization as expected

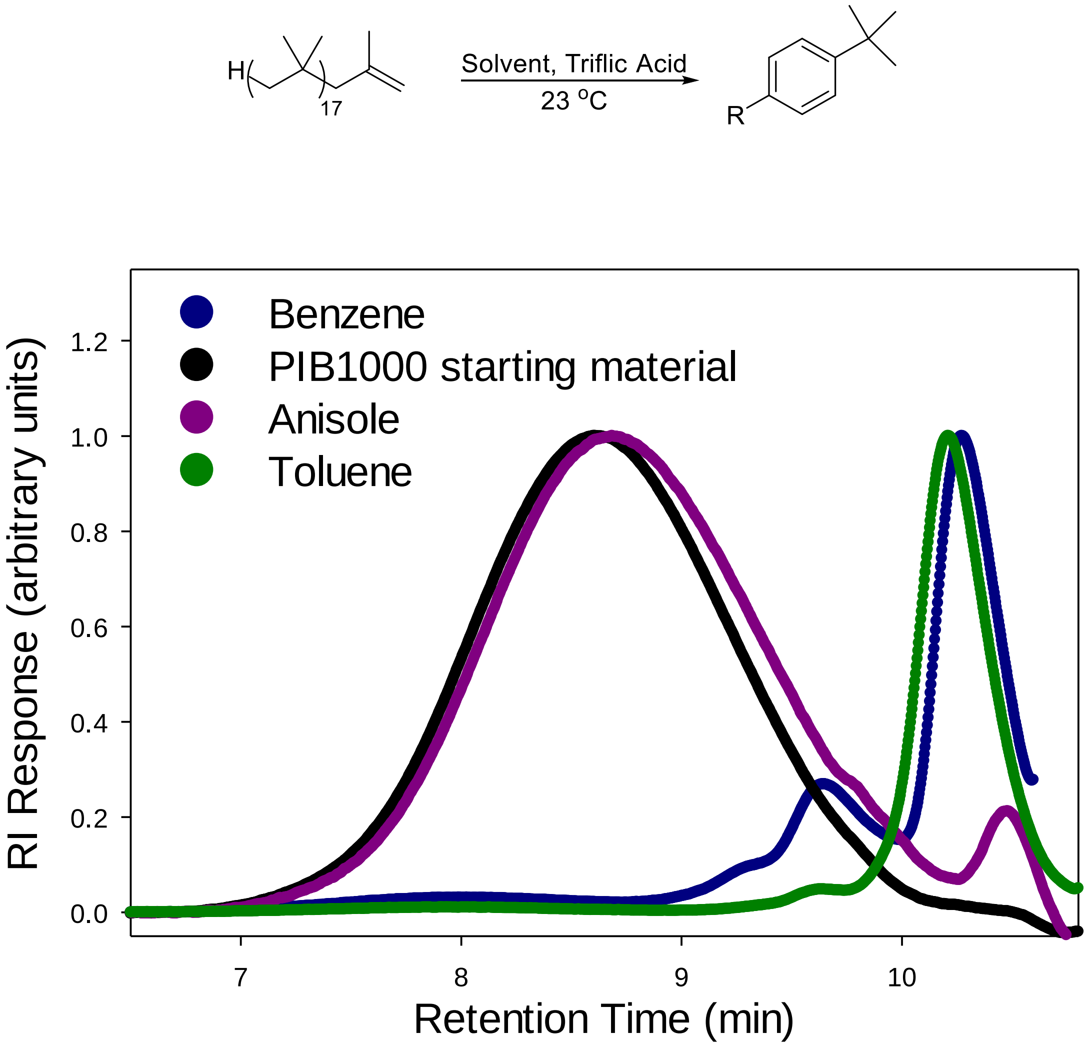


Figure II-20 GPC trace of PIB alkene after degradation using 2 equivalents of triflic acid and stated solvent after 20 hours

In an effort to detect intermediates in this depolymerization process, we sought to slow the depolymerization by cooling the reaction to 0 °C (Figure II-15 and Figure II-17). However, even at this reduced temperature, the chains were completely depolymerized within the first minute. In order to see what effect the concentrations of the acid and polymer have on the depolymerization, we diluted the reaction tenfold to 60 mL of benzene or toluene (Figure II-21 and Figure II-22). We hypothesized this dilution may slow the reaction enough to see intermediates in the depolymerization via GPC. While the dilution does indeed slow the rate of depolymerization, no intermediate molecular weight materials were detected. Thus, the individual polymer chains do not appear to shorten as a group. Rather it appears that when an initial chain begins depolymerizing, it fully depolymerizes. This is illustrated with PIB_{1000} where the peaks for the starting material decrease without any shift in elution time or peak broadening in either the toluene or benzene reaction. The only other effect of dilution was that conversion of the disubstituted to mono-substituted arene occurred to a lesser extent.

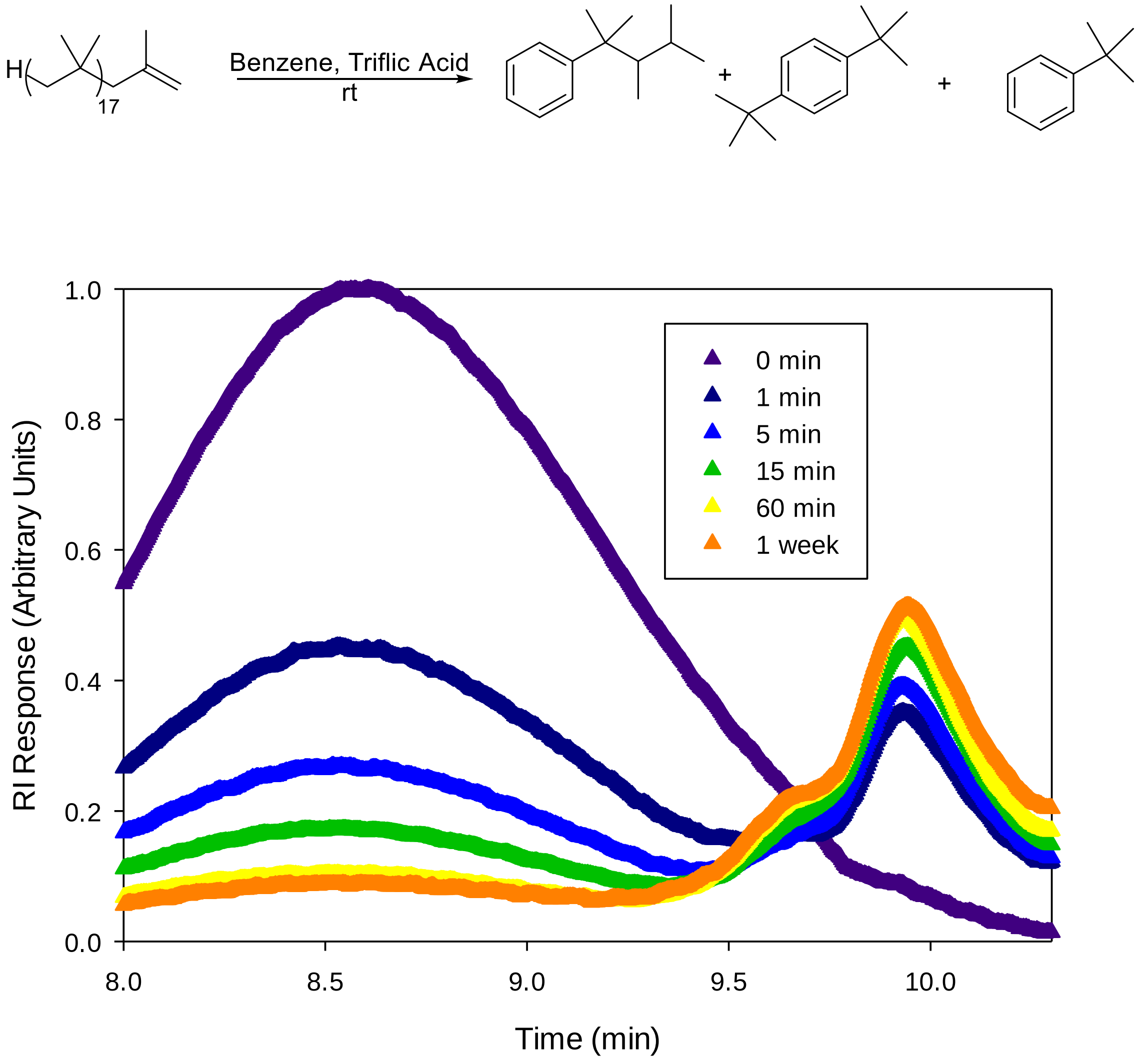


Figure II-21 Depolymerization of 1 g PIB_{1000} alkene using 2 equivalents of triflic acid in 60 mL of benzene over time

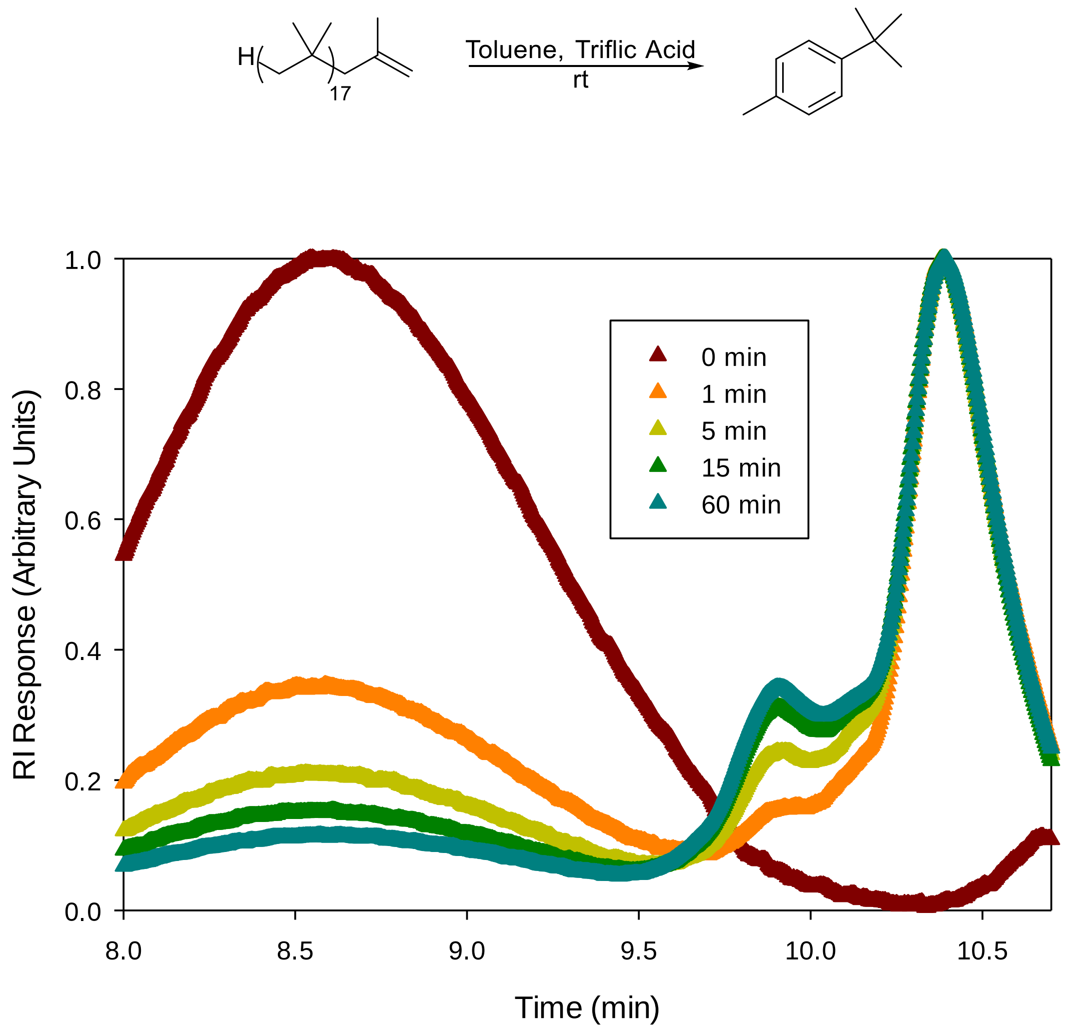


Figure II-22 Depolymerization of 1 g PIB$_{1000}$ alkene using 2 equivalents of triflic acid in 60 mL of toluene over time.

We also studied a depolymerization in the presence of a reduced amount of benzene (Figure II-23). For this reaction, we used 1 g of PIB with 2 equivalents of triflic acid at room temperature, but only one or two tenths of an equivalent of benzene rather than the hundreds of equivalents that had been used before. As seen below, the depolymerization is still complete even in the presence of even a small amount of benzene. The only clear difference between these two trials is the amount of the 1,4-di-

tert-butylbenzene formed. As expected, more of the 1,4-di-substituted benzene is formed in the presence of 0.1 equivalents of benzene (relative to the end group) as there is less benzene available to consume any *tert*-butyl cations formed by ipso substitution of 1,4-di-*tert*-butylbenzene. When 0.2 equivalents of benzene were used, more unreacted benzene is present as well as less of the disubstituted species as expected when increasing the amount of benzene.

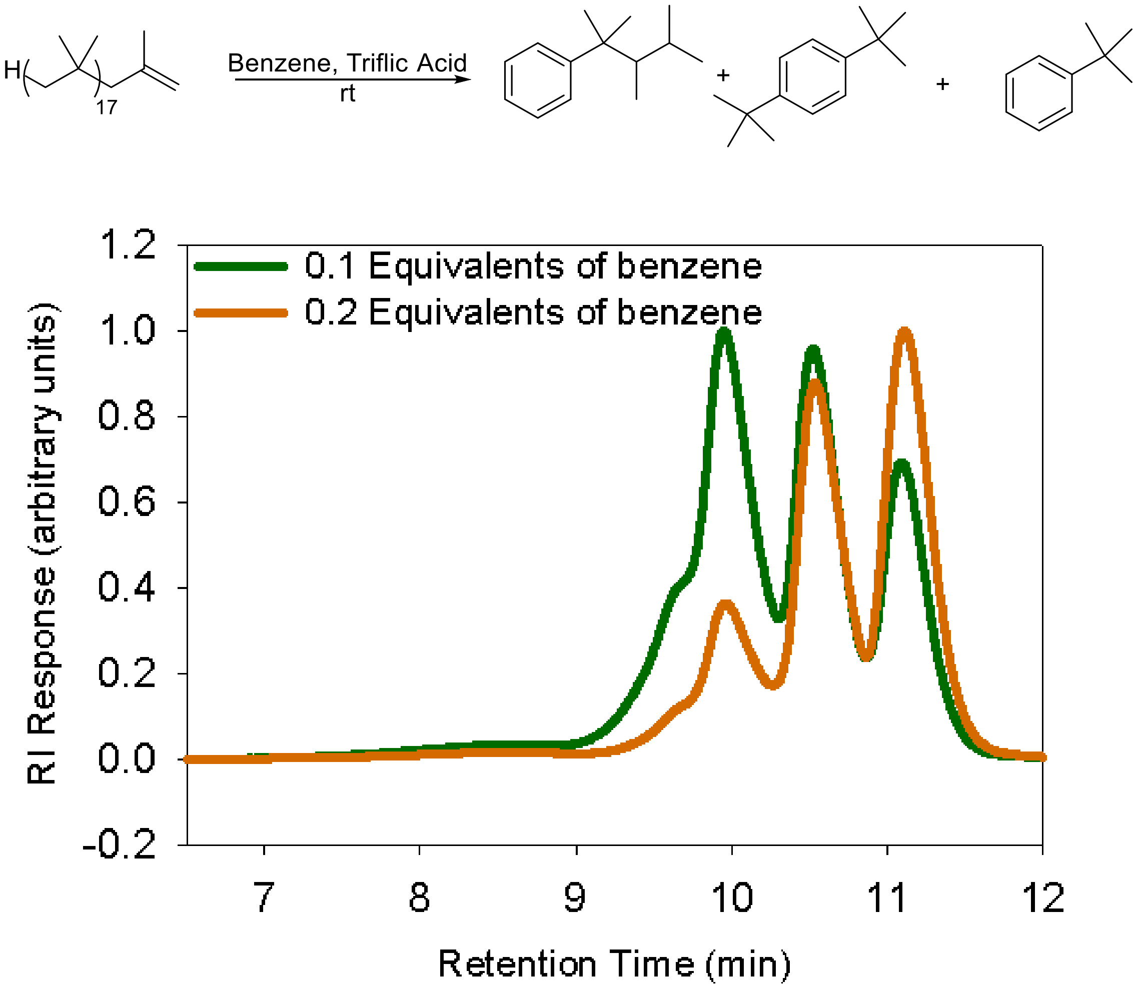
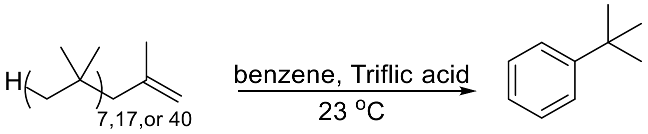


Figure II-23 Depolymerization of 1 g PIB$_{1000}$ using 2.2 equivalents of triflic acid in either 0.1 or 0.2 equivalents of benzene at room temperature. The peak at 11.2 minutes is unreacted benzene.

We further studied these depolymerizations using three different M_n of PIB alkene, 450, 1000 and 2300 Da (Figure II-24). As expected, all three molecular weights of this PIB-alkene completely depolymerize to the *tert*-butylbenzene after 20 hours. Further confirming that this is an end group driven process that thus likely gives the same intermediates and importantly, leads to the same products.



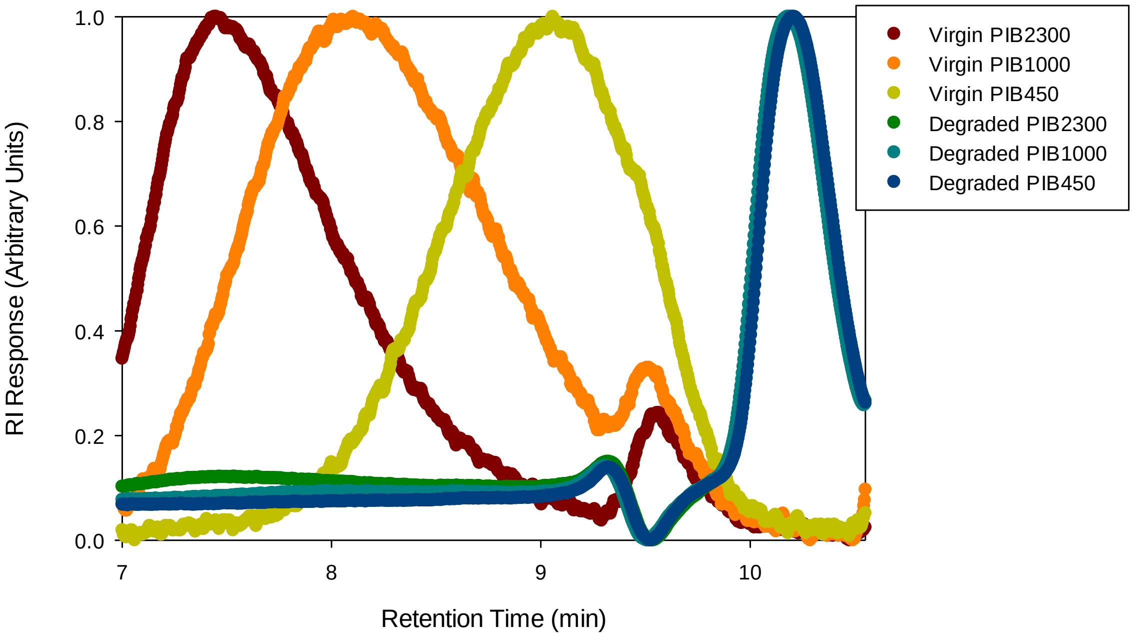
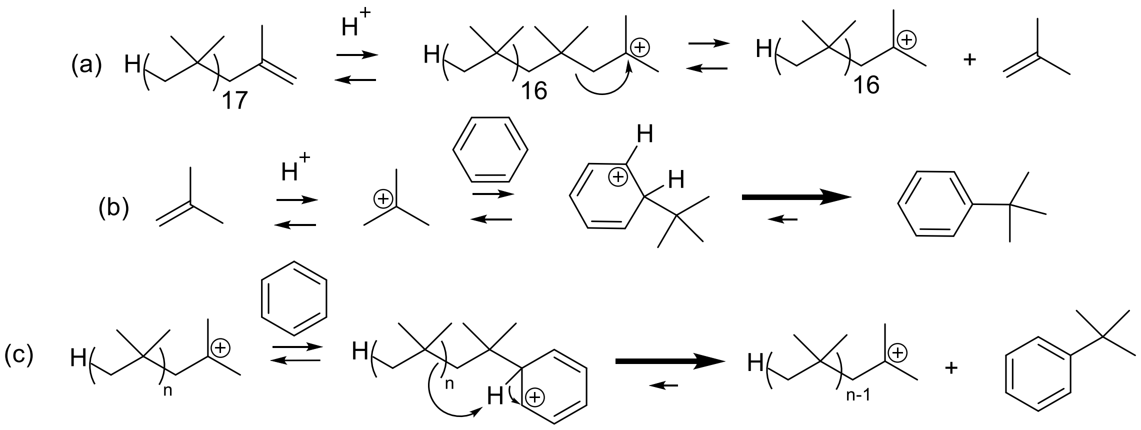


Figure II-24 GPC trace of three different molecular weights of PIB degrading in the presence of 2.2 equivalents of triflic acid and 60 mL of benzene after 20 hours at room temperature.

The above data has led me to the mechanism proposed in Scheme 1. The reaction does not proceed either with weak acids or in the absence of acid so the PIB alkene must first be protonated. Even if the protonated PIB were attacked by the solvent, this step is reversible as shown by the exchange of the phenol and anisole end groups of the PIB. Further, we propose that the small amount of isobutylene that could be formed via an elimination process could then be protonated and attacked by the solvent to lead to the tert-butylbenzene. This process can happen a second time to lead to the 1,4-di-*tert*-butyl arene which is likely the fastest forming product, as the initial addition of the tert-butyl group activates the ring at the para position. Additionally the polymer chain degrades so quickly that it is plausible the butylated arenes do not have time to leave the local sphere before additional equivalents of the butyl cation are present and subsequently attacked. As previously discussed, the ipso substitution of 1,4-di-*tert*-butylbenzene generates *tert*-butylbenzene and a *tert*-butyl cation. Reaction of the *tert*-butyl cation with a second equivalent of benzene solvent forms a second equivalent of *tert*-butylbenzene.



Scheme 1 (a) Proposed mechanism of depolymerization with (b) subsequent attack of the protonated isobutylene to form the major *tert*-butyl product or (c) alternative depolymerization mechanism

As discussed in the previous chapter with polymerizations, depolymerizations are governed by the Gibbs free energy (ΔG) of the reaction. Normally depolymerizations are driven by entropy. In depolymerizations, a polymer with a degree of polymerization N forms N monomers, leading to a favorable ΔS. However, the bonds in the polymer are typically stronger than the bonds in the monomer. This leads to a ΔG that favors polymerization. It also means that the most common strategy for depolymerization is to carry it out under conditions where the –TΔS term outweighs the ΔH term in the Gibbs equation. This is illustrated by the ceiling temperature associated with many polymerization reactions.

However, for the depolymerizations above, the monomer units being generated are consumed by equivalents of solvent. Thus, as N+1 molecules are going to N molecules, this should have a small entropy change (ΔS) in either the positive or negative direction. We thus can approximate the ΔG of the reaction as the enthalpy of the reaction (ΔH).

I used values available in the literature, to calculate the ΔH to confirm this in three ways (Equation II-1, Equation II-2, and Equation II-3). In the first, I used available data to find the total enthalpy change for polyisobutylene and benzene going to *tert*-butylbenzene. In the second, I compared the difference in energy between isobutylene going to polyisobutylene with isobutylene and benzene going to *tert*-butylbenzene. In the third approach, I used the difference between the heat of formation of *tert*-butylbenzene in the gas phase and the heat of polymerization in solution as an approximation for the polymerization in the gas phase. All three of these methods gave similar values and all of them confirmed that the reaction is indeed energetically downhill by about 7 kcal/mol.

1. $\Delta H_{\text{reaction}} = \Delta_f H^{\circ}_{\text{tert-butylbenzene}}(\text{l}) - (\Delta_f H^{\circ}_{\text{PIB}}\ (\text{l}) + \Delta_f H^{\circ}_{\text{benzene}}(\text{l}))$

1. $\Delta H_{\text{reaction}} = -7.3$ kcal/mol

Equation II-1 Calculation of ΔH using the heats of formation of starting materials and products

2. $\Delta H_{\text{reaction}} = -\Delta H_{\text{polymerization}}(\text{l-l}) + \Delta_{\text{vap}} H^{\circ}_{\text{isobutylene}} - \Delta_f H^{\circ}_{\text{isobutylene}}\ (\text{g}) + \Delta_{\text{vap}} H^{\circ}_{\text{benzene}} - \Delta_f H^{\circ}_{\text{benzene}}(\text{g}) + \Delta_f H^{\circ}_{\textit{tert}\text{-butylbenzene}}\ (\text{g}) - \Delta_{\text{vap}} H^{\circ}_{\textit{tert}\text{-butylbenzene}}$

2. $\Delta H_{\text{reaction}} = -6.1$kcal/mol

Equation II-2 Calculation of ΔH using the difference in energy between isobutylene polymerizing and isobutylene being attacked by benzene to give *tert*-butylbenzene.

3. $\Delta H_{\text{reaction}} = -\Delta_f H^{\circ}_{\text{isobutylene}}\ (\text{g}) - \Delta_f H^{\circ}_{\text{benzene}}(\text{g}) + \Delta_f H^{\circ}_{\text{tert-butylbenzene}}(\text{g}) - \Delta H_{\text{polymerization(in solution)}}$

3. $\Delta H_{\text{reaction}} = -8.1$ kcal/mol

Equation II-3 Calculation of ΔH using the difference between the heat of formation of *tert*-butylbenzene, benzene, isobutylene and an approximation of heat of polymerization all in the gas phase.

This enthalpy driven depolymerization can also be considered in a simpler way by comparing the types of bonds being broken in the PIB with the *tert*-butyl-arene bond. The sigma bond in the polymer is a bond formed by Csp3-Csp3 orbitals. In the product *tert*-butylbenzene, the C-C bond is formed by a Csp2-Csp3 orbital. The latter C-C bond is stronger. However, while this qualitative analysis is simplistically attractive, it is complicated by the fact that the C-H bond of benzene is ca. 5-10 kcal/mol stronger than the C-H bon of the primary methyl group of *tert*-butylbenzene. Thus the more formal calculations above provide a better justification for this enthalpically driven depolymerization process.

Conclusion

In conclusion, PIB alkene depolymerizes entirely in the presence of excess triflic acid and suitable arene solvents into predominantly the mono and di-*tert*-butylated arene. This process did not proceed in the presence of any acids that we tested that were weaker than triflic acid. The arene solvent itself is very important for this reaction, as arenes that are too electron rich are protonated, which stops the reaction by solvent leveling of the acid. Conversely, arenes that are too electron poor do not make good nucleophiles for this process. Additionally the solvent is required because the reaction of solvent with the isobutylene equivalents drives the reaction not only by Le Chatelier's Principle, but also energetically, as it is the exothermic step of this depolymerization reaction. End group studies showed that the mechanism of depolymerization must be end driven rather than degrading via random cleavage throughout the chain, as hydrogenated PIB does not degrade. Time trials were conducted at reduced temperatures, but the polymer depolymerized completely within the five minutes, showing that the reaction is kinetically very fast, but not allowing us to measure the actual rate. When the reaction was diluted, the depolymerization overall was slowed, but it appears that depolymerization of individual chains was still very rapid, because there was no increase in elution time observed that would have been expected in a chain shortening process. Furthermore, the di-*tert*-butyl arenes can be observed, in the presence of an excess of acid and solvent, to form the mono-*tert*-butyl arene product by known ipso substitution. This process has shown that the depolymerization of PIB can be accomplished at ambient or even sub-ambient temperature in the presence of triflic acid and suitable arene solvents.

CHAPTER III

PIB BOUND SULFONIC ACIDS IN PAOS, A RECYCLABLE CATALYST/SOLVENT SYSTEM*

Introduction

Homogeneous and heterogeneous acid catalysts are some of the most often used catalysts in organic chemistry. They find ubiquitous uses in reactions such as the formation of acetals and ketals, esters, and multi-component condensations and in other chemistry where a neutral substrate is activated by formation of a Lewis acid-Lewis base couple. There are literally dozens if not hundreds of examples of such acid catalysts. They include soluble and insoluble Lewis acids like the metals centers in a zeolite or the Al center in aluminum trichloride ($AlCl_3$). Soluble and insoluble Brønsted acid catalysts are equally common. The work in this chapter is focused on Brønsted acid catalysts.

Examples of soluble Brønsted acid catalysts used in industry include catalysts like phosphoric acid, perchloric acid, nitric acid, and sulfuric acid. Hydrochloric acid (HCl) is another Brønsted acid often used in industry. For example, it is used in steel pickling to clean the surfaces of metals. While it can be used effectively, it has to be disposed of at the end of the reaction – it is not recyclable. That is a problem because the waste streams can be significant in terms of volume since the catalyst is present in a dilute solution that is typically neutralized with another solution of base before the actual

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disposal process. Concentrated HCl also is a hazardous material with volatile HCl gas posing a safety issue. Another example of a soluble Brønsted acid is hydrofluoric acid (HF). HF is a compound with well-known toxicity. It has a high vapor pressure and dissolves glass and many metals so it must be used in nickel/copper alloy apparatus. However, HF is still widely used as an acid catalyst. HF also has the odd distinction of being part of a Green Chemistry award winning process where it replaces $AlCl_3$, a non-recyclable acid, in an electrophilic aromatic substitution (Figure III-1). This process, which is still being carried out in Bishop, TX, has been used to make 4′-*iso*butylacetophenone, a key intermediate for Ibuprofen (2-[4-(2-methylpropyl)phenyl]propionic acid) and an intermediate used in making 4-hydroxystyrene esters, photo-acid sensitive materials used to make memory chips.

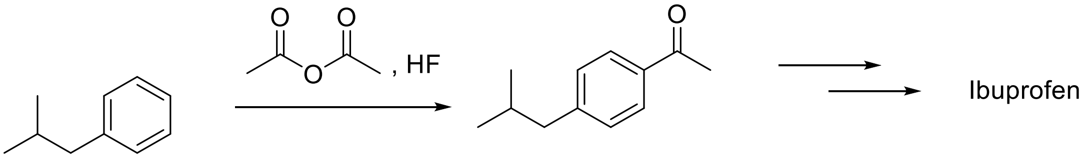


Figure III-1 First step in the synthesis of Ibuprofen, catalyzed by recycled HF.

Perhaps the most classic soluble Brønsted acid catalysts are sulfuric acid (H_2SO_4) and analogs of sulfuric acid like methanesulfonic acid, *p*-toluenesulfonic acid and trifluoromethanesulfonic acid. While alkyl- and arylsulfonic acid catalysts have been in use for nearly 70 years, they continue to be of interest and are widely used today.[77] This is in part due to their solubility in organic solvents, coupled with the fact that they are not oxidants like simpler H_2SO_4, which can act as an oxidant while being reduced to form sulfur dioxide and water. They also hold the advantage of being nonvolatile, which helps to prevent their solutions from evolving toxic gases like those that can be given off from hydrochloric acid or hydrofluoric acid solutions. However, a homogeneous sulfonic acid catalyst or a sulfuric acid catalyst is typically not recycled and disposal of the acid solutions of these catalysts generates chemical wastes that have to be disposed of as discussed above.

While methanesulfonic acid has been described as a green reagent because it is a part of the sulfur cycle, and thus a sustainable reagent,[78] there are still significant efforts to make recyclable analogs of it in order to reduce waste. For example, commercially available camphorsulfonic acid has been used as a catalyst for the lab scale synthesis of coumarin derivatives via an acid-catalyzed aldol condensation (Figure III-2).[79] After the reaction, the products precipitate, and can be removed by filtration, with the filtrate being concentrated to recover the starting camphor sulfonic acid which can be reused.

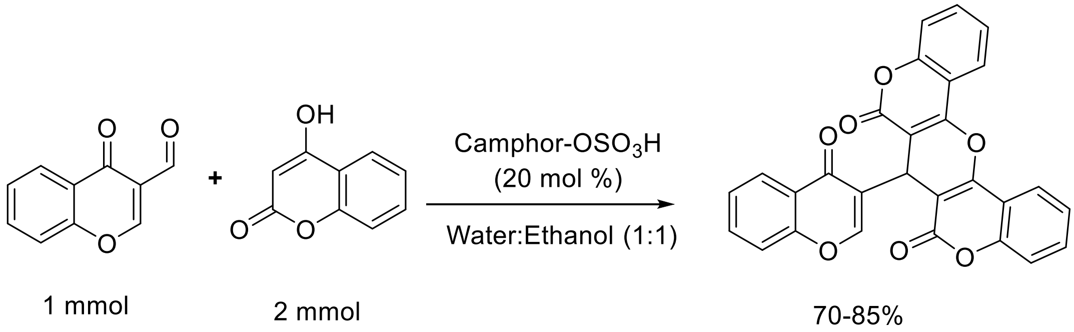


Figure III-2 Camphorsulfonic acid catalyzed synthesis of coumarin derivative in 5 mL of ethanol:water. The solvent and catalyst were both reused 4 times to give the product in 70-85% yield.

Brønsted acid ionic liquids (BAIL) are another example of recyclable homogeneous sulfonic acid catalysts. BAIL have been used in the acetylation of glycerol with acetone (Figure III-3).[80] In this case, 2.7 mol% of the BAIL was added to a mixture of glycerol and acetone (1:15 molar ratio) and stirred for 15 minutes. The BAIL was then separated from the products by precipitation of the BAIL into excess diethyl ether, and centrifugation followed by washing the BAIL several times with diethyl ether and drying under reduced pressure. The BAIL can then be reused upon addition of fresh acetone and glycerol at least 4 times while maintaining >90% conversion.

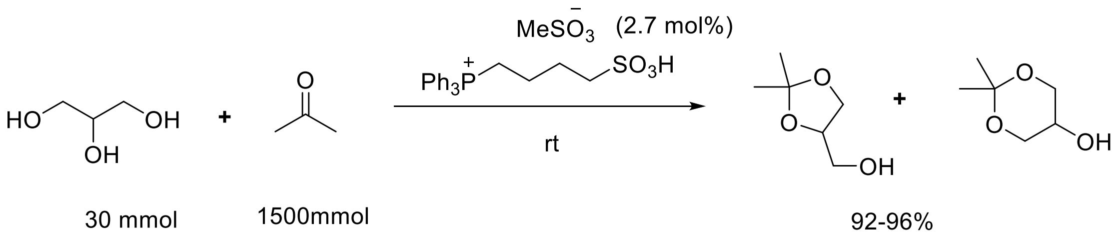


Figure III-3 BAIL catalyzed acetylation of 30 mmol of glycerol with 1500 mmol of acetone to give 92-96% conversion to the ketal.

However, while these two examples illustrate possible ways to recycle alkyl sulfonic acid catalysts, the recycling schemes involved generate a lot of solvent waste. An alternative approach is to make derivatives of sulfuric acid that are polymer bound. Such heterogeneous catalysts could thus be used in flow and separated from products or simply recovered by filtration in a batch reaction if the products were soluble. For example, polystyrene (PS) can be used to make commercially available, hydrophobic versions of toluenesulfonic acid. After completion of the reaction these heterogeneous polymer bound sulfonic acids can be separated from the reaction solution by simple filtration. Catalysts of this type, such as Amberlyst, are used on industrial scale to produce materials such as alkylated phenols (Figure III-4).

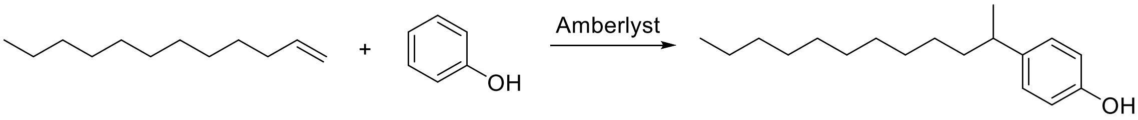


Figure III-4 Amberlyst resin catalyzed synthesis of dodecyl phenol.

Poly(4-styrenesulfonic acid) has also used on an industrial scale to produce *tert*-butyl methyl ether from isobutylene and methanol (Figure III-5). While tens of millions of tons of this gasoline oxygenate were being made in the early 2000s, its production volume has fallen as many countries have outlawed its use as a fuel additive due to environmental and health concerns.

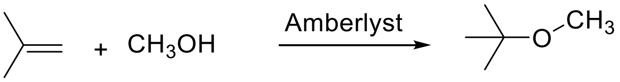


Figure III-5 Amberlyst resin catalyzed synthesis of *tert*-butyl methyl ether.

Although they are not often recycled industrially, these polymer bound acids are often recycled in laboratory scale experiments. For example, Amberlyst 15 has been used to catalyze the formation of a series of sulfones (Figure III-6). After reaction the catalyst can be recycled up to five times by filtration and washing with ethyl acetate.[81]

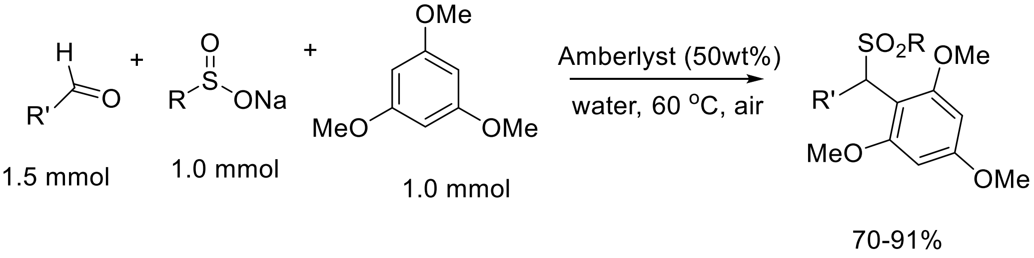


Figure III-6 Amberlyst catalyzed formation of sulfone products. R' groups include H, phenyl, methyl, benzyl, *p*-nitrophenyl, and *o*-hydroxyphenyl. R groups include ethyl, phenyl, and *p*-chlorophenyl.

Soluble polymer-bound analogs of a sulfonic acid can be made simply by reaction of a terminal hydroxyl PEG with chlorosulfonic acid. These PEG-OSO_3H catalysts have been used in an assortment of chemistry such as the catalysis of acetal formation from aldehydes and acetic anhydride (Figure III-7). The catalyst can be subsequently removed by simple extraction with water. After being dried, the catalyst can be reused at least 4 times. [82]

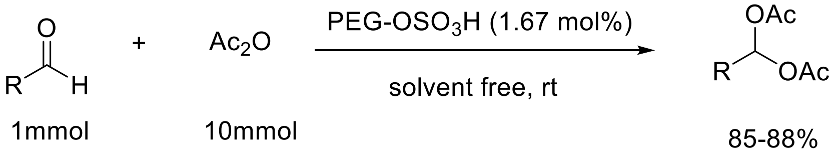


Figure III-7 PEG-OSO_3H catalyzed conversion using 1 mmol of aldehyde and 10 mmol acetic anhydride to form acetic acetals. R groups for aldehydes include phenyl, *p*-nitrophenyl, *p*-bromophenyl, *p*-methoxyphenyl, and pentyl groups.

Another approach to making a recyclable heterogeneous Brønsted acid catalyst is to use an inorganic support. This is illustrated by an acid functionalized periodic mesoporous organo-silica (PMO) which has been synthesized *in-situ*, or using post polymerization modifications (Figure III-8). This acidic inorganic resin has been used as a heterogeneous catalyst for esterifications, such as that of acetic acid with benzyl alcohol under solvent free conditions at 120 °C. After the esterification reaction was complete, the acid catalyst was removed by filtration, washed with acetone and dried at 110 °C. It could be reused at least 5 times with no observable loss of catalytic activity.[83]

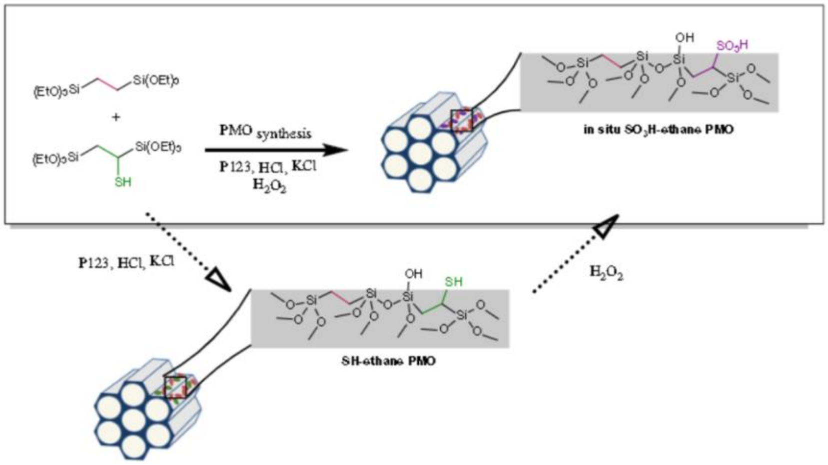


Figure III-8 Synthesis of sulfonic acid modified PMO *in-situ* or in a two-step process. Reprinted with permission from (82).

An example of a heterogeneous alkyl hydrogen sulfate acid catalyst that is an alternative to the PEG hydrogen sulfate catalyst discussed in Figure III-7 above has also been described. This catalyst uses a naturally derived cellulose polymer as a support and is a somewhat greener example of an insoluble polymer bound catalyst than the poly(4-styrenesulfonic acid) discussed above. This cellulose hydrogen sulfate catalyst (Cellulose-OSO_3H) is prepared from cellulose using chlorosulfonic acid. This catalyst was used in a Nazarov cyclization of a dieneone to test its recyclability (Figure III-9).

The catalyst was then removed by filtration, washed twice with ethanol and dried at 60 °C. The catalyst could be reused at least 5 times with no detectable loss of catalytic activity.[84]

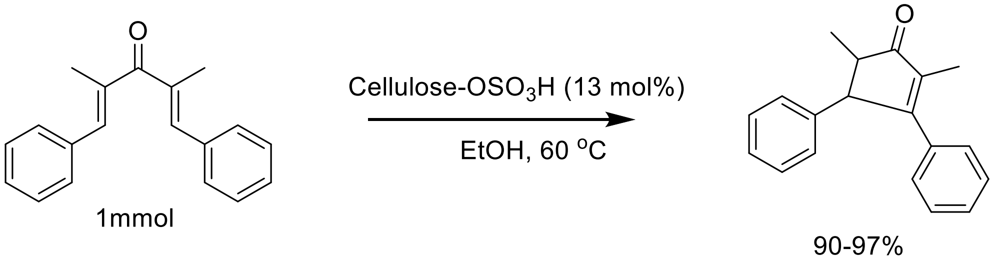


Figure III-9 Cellulose-OSO$_3$H (13 mol%) catalyzed Nazarov-cyclization reaction of 1 mmol of a dieneone in 10 mL of ethanol that can be recycled at least 5 times.

Polymeric analogs of a perfluorosulfonic acid have also been prepared. Such sulfonic acids are more acidic than their hydrocarbon analogs in the same way that trifluoromethanesulfonic acid (the acid used in PIB depolymerization in Chapter 1) is a stronger than methanesulfonic acid. The best known example of this sort of insoluble perfluorosulfonic acid is Nafion-H. This perfluorinated polymer bound sulfonic acid is prepared from a copolymer of tetrafluoroethylene and a perfluoro(vinyl ether) monomer that has a terminal SO$_2$F. The polymer bound super acid is then formed by hydrolysis of the -SO$_2$F groups. It can be used in a variety of reactions as a heterogeneous catalyst. An example is the Mannich reaction where the acid can also be recycled four times by filtration without the need for further purification (Figure III-10).[85]

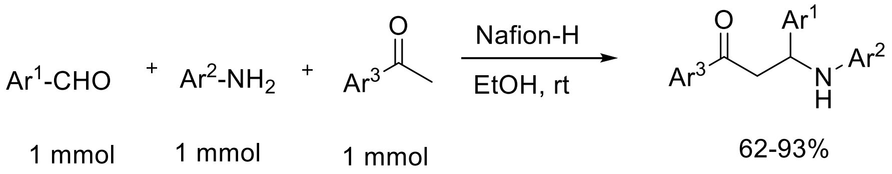


Figure III-10 Use of Nafion-H resin in ethanol to catalyze multicomponent condensation reactions. Ar^1 groups include phenyl and *p*-methoxyphenyl. Ar^2 groups include phenyl, tolyl, *p*-methoxyphenyl, and *m*-nitrophenyl. Ar^3 groups include phenyl and tolyl.

All of the above acid catalysts have several characteristics that make them desirable. For instance, they all give good yields of desired products, and many can be recycled, although the recycling procedures, especially in the case of soluble acid catalysts, are not always efficient. However there are still drawbacks to these catalysts. The majority of them are heterogeneous catalysts, which have the inherent drawback of their reactivity being dependent on the surface area of the catalyst. In other cases, there are potential problems inherent in the catalysts. For example, BAILs have toxicity issues and sometimes require column chromatography in the product separation step.

In the work below, I describe how I prepared polyisobutylene bound alkyl- and arylsulfonic acid catalysts that are similar to methanesulfonic acid and *p*-toluenesulfonic acid catalysts respectively. However, while these materials have structural similarities that should make them roughly equivalent in terms of acidity, the PIB-bound materials are soluble in alkanes and in a fully recyclable PAO alkane solvent. In the studies below, I've used a series of sulfonic acid catalyzed processes to show that these PIB-bound acid catalysts have equivalent efficacy as catalysts, affording products in comparable conversions and/or yields. I also explored the potential of these PAO solvent systems to perturb the equilibria that are often present in an acid catalyzed process that generated water as a product. Finally, I explored the viability of exploiting the low volatility of a PIB-bound sulfonic acid and a PAO solvent as a means of separating a volatile product.

The first Principle of Green Chemistry[86] is waste prevention. While it is often discussed in the use of reagents and catalysts, waste prevention is important in the use of solvents as well. While the catalyst often receives more focus, likely due to the precious nature of many catalysts, the solvent accounts for a far larger portion of the waste of a reaction. While some reactions can be run in a solvent free environment, solvents are commonly needed in order to control the concentrations of reactions as well as serving as a thermal sink in order to dissipate energy from exothermic reactions or provide it for reactions that are endothermic.

Because solvents are often required, it is a good practice to look at ways to reduce the magnitude of waste from their use. For example, one problem is that most organic solvents are eventually burned in disposal, releasing large amounts of carbon dioxide. The use of bioderived solvents in place of petrochemical derived solvents addresses this issue. However, an alternative way to reduce the waste generated by the use of solvents is by their reuse in additional reactions. Many solvents are volatile. While this can simplify their removal from desired products, this makes their recycling problematic due to evaporation of the solvent and subsequent loss. In order to address this problem, easily separable and recyclable higher boiling solvents and those with low vapor pressures are required.

One way to make low vapor pressure solvents is through the use of ionic liquids as solvents. Ionic liquids are ionic solvents that melt at low temperature, which allows them to be of use as solvents, often even at ambient temperature. These materials usually have the low vapor pressure that makes them ideal for recycling. Moreover, ionic liquids can often be separated from desired products by simple extraction. These materials do however have drawbacks. As mentioned above, in connection with BAIL, many ionic liquids are toxic. In addition, the subsequent disposal of water or other contaminated extracting solvents used with ionic liquids can be problematic.

An alternative way to achieve a low vapor pressure and high boiling temperature is to use oligomeric or polymeric solvents. Polymers have been used as solvents before. For instance, PEG (of varying molecular weights), can be used as a solvent. PEG is by far the most common example of such a polymeric solvent. In one example, PEG_{400} was used as a solvent for a Suzuki coupling reaction after which the catalyst and solvent were recycled (Figure III-11). Five reaction cycles were effected without loss of solvent or without loss of catalyst activity.[87] In this case, the products were removed from the solvent by extraction with diethyl ether. While this strategy works, it has the drawback that polar products can be difficult to remove from PEG. PEG may also leach into polar products and the separations typically use a large excess of diethyl ether.

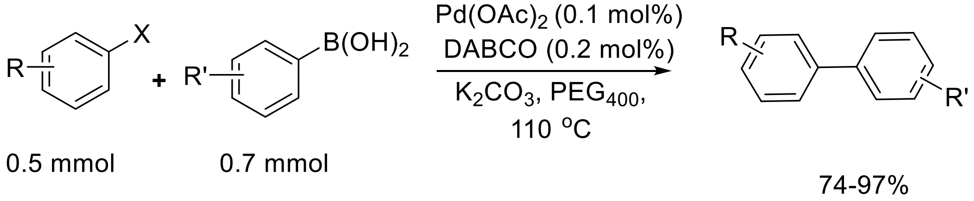


Figure III-11 Palladium catalyzed Suzuki coupling in 2 grams of PEG_{400} solvent at 110 °C. R groups include 4-nitro, 3-nitro, H, 4-methoxy, and 4-acetyl. X groups include I and Br. R' groups include 4-F, H, 4-trifluoromethyl, 4-chloro, and 4-methoxy.

While PEG use in a reaction like Figure III-11 demonstrates that polymers or oligomers can function as a polymeric solvent, our group has demonstrated that hydrocarbon oligomers can be solvents too and that hydrocarbon oligomer bound catalysts in these hydrocarbon oligomer solvents can be recycled. For example, PE oligomers can serve as a polymeric solvent. However, if PE is to be used as a solvent, the PE oligomer has to be heated and the solvent that forms is viscous. PIB or a hydrogenated PIB like the one I made in Chapter 2 is an alternative hydrocarbon that is liquid at room temperature. However, PIB of even low molecular weight is too viscous to use as a solvent for most applications. This issue can be addressed in part by mixing PIB with a non-viscous cosolvent to reduce the solvent mixture's viscosity. However, while we have explored the addition of PIB to heptane in order to improve the separation of the alkane solvent from polar solvents that would still entail using a volatile cosolvent (heptane) and I wanted to avoid that in the acid catalysis schemes I was going to investigate.

Fortunately, our group has shown that less viscous poly(α-olefins) (PAOs) that are fully hydrogenated dimers, trimers and tetramers of 1-decene or 1-dodecene can serve as oligomeric analogs of heptane and as solvents. These PAOs are available with a variety of M_n values and have flash points and viscosities as listed in Table III-1. Examples of lower molecular weight versions listed here have viscosities that are somewhat less or slightly greater than solvents like ethylene glycol or common materials like olive oil - viscosities that I think can be well tolerated in many syntheses.

Table III-1 Molecular weights and flash points of various PAOs.

	Kinematic Viscosity at 40 °C (cSt)	Flash Point (°C)
PAO_{283}	5.54	165
PAO_{432}	16.68	213
PAO_{570}	30.89	235
PAO_{1785}	64.50	270

PAOs could be useful in my studies of new recyclable Brønsted acid catalysts for several reasons. First, PAOs are non-volatile, high boiling solvents - this will prevent their loss in recycling reactions regardless of reaction temperature. As discussed in the introduction, Malinski and Bergbreiter also demonstrated that this causes the solvent to be particularly nonflammable, making it a safer laboratory solvent because of its high flash point. Second, the highly nonpolar nature of PAOs facilitates liquid/liquid separation. PAOs for example separate cleanly from polar solvents such as acetonitrile. This provides a way to nearly quantitatively isolate polar products from a PAO phase after the reaction is complete. Third, PAOs are also inexpensive and commercially available, which is a requirement if they are to become widely used as solvents. Fourth, as was true in my colleagues' work, it is likely I would find cases where products are insoluble, but starting materials are soluble, allowing for solid/liquid separations of products from a recyclable catalyst/solvent system. Fifth, while these solvents, like other nonpolar solvents sometimes poorly solubilize species, this could be an advantage. For example, I hypothesize below that I could take advantage of this fact and use it to drive water out of the reaction solution and thus improve the yield of equilibria in condensation reactions by Le Chatelier's Principle. Sixth, Thavornpradit, Killough, and Bergbreiter have already demonstrated that the use of cosolvents in PAOs can facilitate reactions (as discussed in the introduction).This can broaden the applicability of PAOs as a solvent if I encountered cases where the reagents prove insoluble in PAOs. Finally, with the use of a properly phase anchored acid catalyst; these PAOs make it possible to examine acid catalyzed reactions in highly nonpolar media to see if the reaction rates or even products may change.

Results and Discussion

While many different molecular weights of these PAOs are available (Table III-1), these studies predominantly use PAO_{432} because it has a good balance of viscosity for a solvent, while also having little to no leaching into polar solvents. However, conventional strong acids such as methanesulfonic acid or *p*-toluenesulfonic acid have little to no solubility in PAOs or in PAO_{432} in particular. Thus, in order to examine homogeneous strong acid chemistry in these solvents, I had to synthesize nonpolar phase anchored sulfonic acid catalysts. Our group has significant experience using PIB for the purpose of immobilizing catalysts in hydrocarbons and I thus chose PIB as my phase anchor of choice. A methanesulfonic acid analog of PIB, **2** could be synthesized from alkene terminated PIB$_{1000}$ **1** using a known thio-ene reaction followed by a known oxidation to give the sulfonic acid. However, our initial attempts to make PIB-aryl sulfonic acid through the use of benzene and a strong acid followed by sulfonation failed due to depolymerization as discussed in the previous chapter. To this end, using known chemistry published by our group, we synthesized a PIB-bound anisole and followed this reaction with sulfonation in order to obtain the desired PIB bound analog **3** of p-toluenesulfonic acid from alkene terminated PIB$_{1000}$ **1** (Figure III-12).

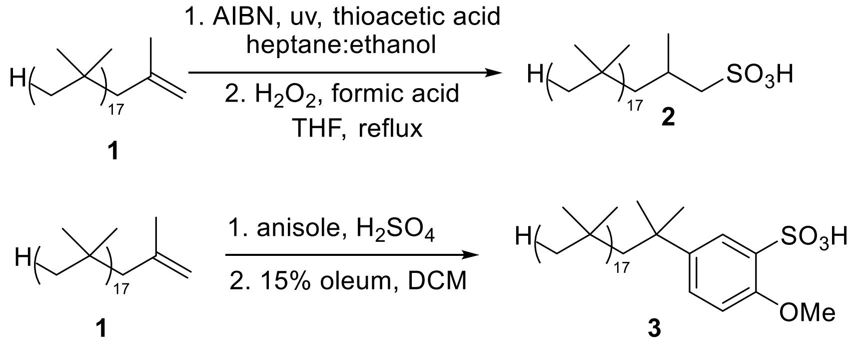


Figure III-12 Synthesis of alkyl and aryl PIB bound sulfonic acids 2 **and** 3**.**

After synthesis of these acids, both were tested for their acid content by titration using standardized sodium hydroxide and a phenolphthalein indicator. The acid **2** had an acid content of 0.74 mmol –SO_3H/g of PIB which was consistent with a molecular weight of 1400 Da, while **3** gave 0.62 mmol –SO_3H/g of PIB consistent with a molecular weight of 1600 Da. In both cases the M_n values are higher than expected. The reason these M_n values are higher than initially expected, is because the highly polar sulfonic acid group caused the lower molecular weight polymeric catalysts to leach into the acetonitrile phase during workup of the products, skewing the M_n somewhat toward larger polymers. This effect was noted in prior work with PIB-bound phthalocyanine catalysts.[88]

Both PIB bound acids were then tested for their stability to elevated temperatures. To ensure that the acids did not desulfonate at elevated temperature, athermogravimetric analysis was performed. The acids were slowly heated to ~300 °C to see if the loss of -SO_3 would occur before degradation of the polymer backbone. Both analyses (Figure III-13 and Figure III-14) show that the polymers were stable to ~ 170 °C, and did not undergo desulfonation below this temperature. Thus both PIB bound acids could be used below ~150 °C without degradation due to heat.

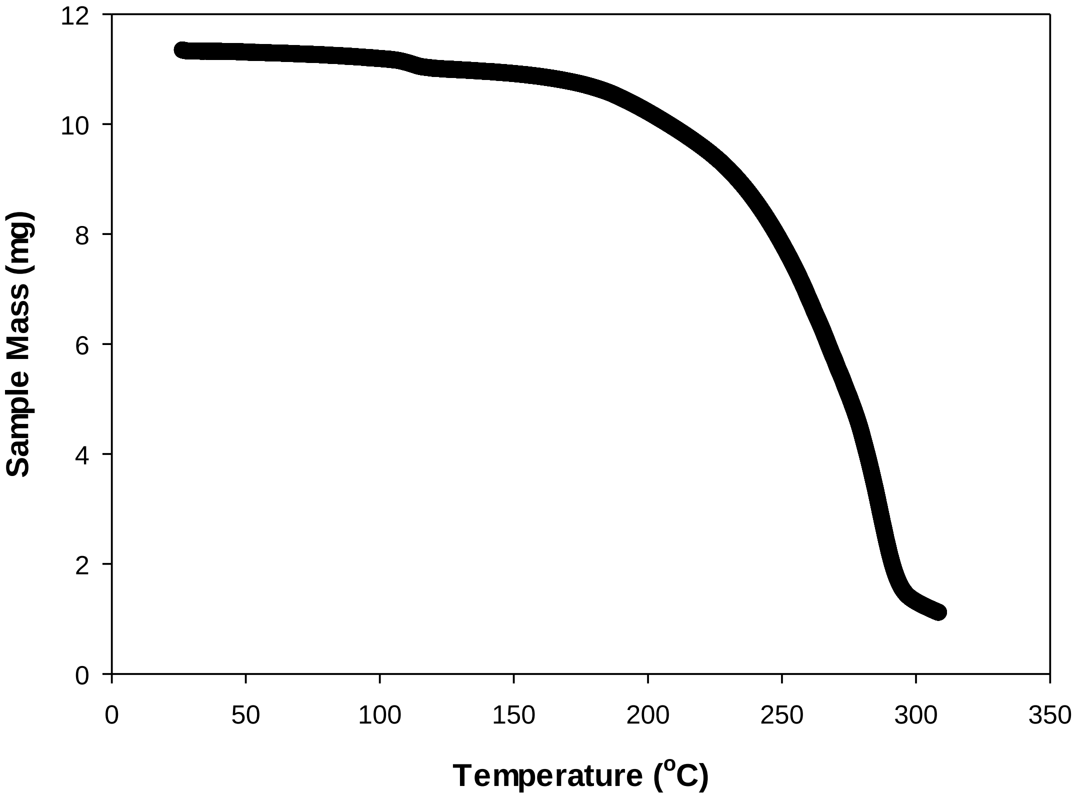


Figure III-13 TGA analysis plot of PIB-bound sulfonic acid 2 showing no desulfonation prior to depolymerization.

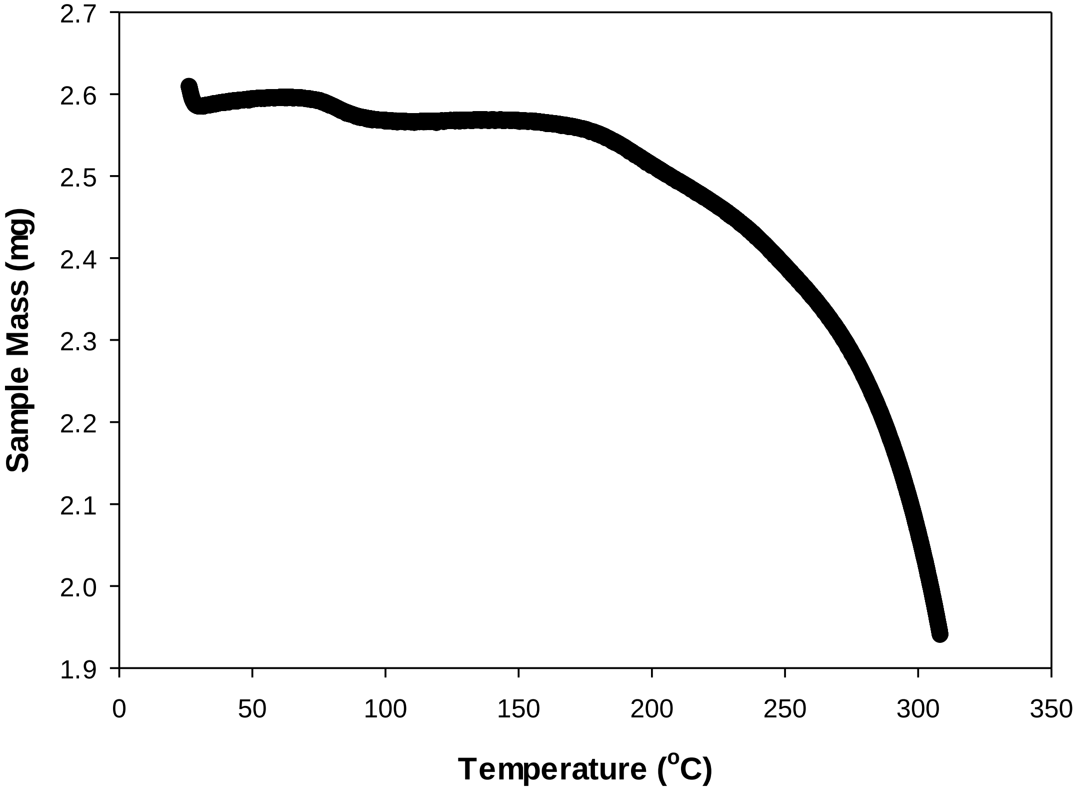


Figure III-14 TGA analysis plot of PIB-bound aromatic sulfonic acid 3 showing no desulfonation prior to depolymerization.

The phase selectivity of these polymer bound acids was then tested using a *para*-methyl red dye **4** and a biphasic PAO_{432}/methanol solvent system (Figure III-15). As shown in Figure III-15, in the absence of acid, the dye is a bright yellow color and exclusively in the top methanol phase (far left). In the presence of a conventional acid (methanesulfonic acid) the dye becomes pink (second from left) and is insoluble in the PAO phase. In the presence of either acids **2** (second from right) or **3** (far right), the dye remains unprotonated in the methanol phase, showing that our acids are indeed phase anchored to the PAO_{432} phase.

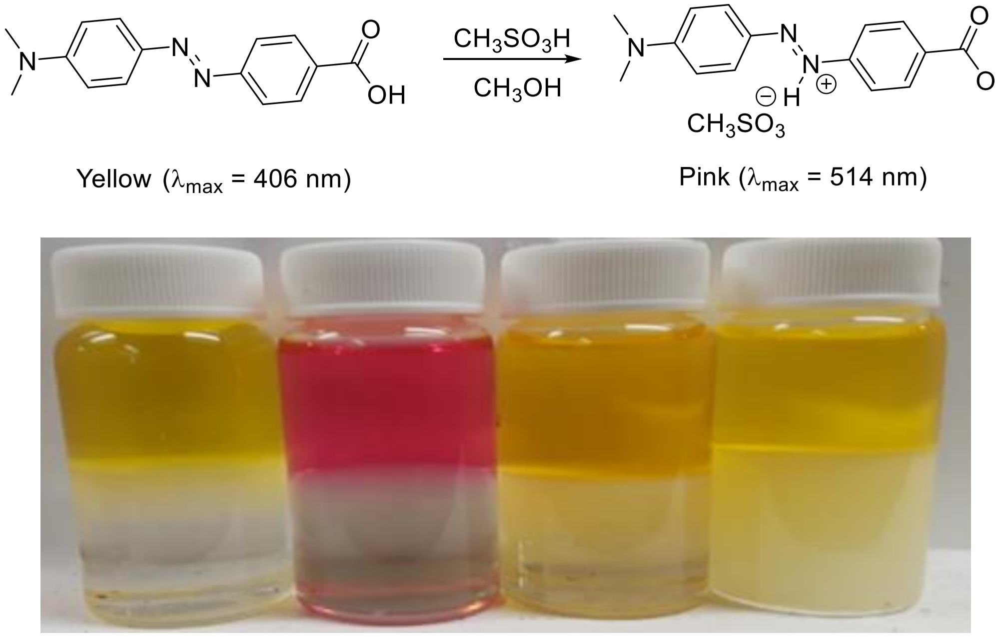


Figure III-15 (far left) *p*-Methyl red 4 **dissolved into methanol above a PAO$_{432}$ phase while, (second from left) *p*-methyl red** 4 **dissolved into methanol with methanesulfonic acid above a PAO$_{432}$, (second from right) *p*-methyl red** 4 **dissolved into methanol above a PAO$_{432}$ phase containing** 2 **and (right) *p*-methyl red** 4 **dissolved into methanol above a PAO$_{432}$ phase containing** 3**.**

PIB bound sulfonic acids **2** and **3** were then tested as catalysts in the reaction of benzyl alcohol with dihydropyran to form an acetal. As part of this experiment, I also compared the recyclability of **2** and **3** to a commercially available lipophilic dodecylbenzenesulfonic acid (Figure III-16). Each acid (5 mol %) was dissolved into 10 mL of heptane because the dodecylbenzenesulfonic acid did not have high solubility in the PAO$_{432}$. Then 1 mmol of benzyl alcohol and 1.2 mmol of dihydropyran (DHP) were added. The reaction was run for one hour and then extracted with 3 mL of acetonitrile followed by the addition of fresh reagents and the process was repeated. Although all three acids initially gave good conversions of >99%, the conversion for reactions using the dodecylbenzenesulfonic acid rapidly decreased after the second cycle, showing that the dodecyl group was not large enough to phase anchor the catalyst in heptane. In contrast, the conversions for reactions using the PIB bound acids **2** and **3** as catalysts remained >85% through 5 cycles suggesting **2** or **3** can be recycled in heptane.

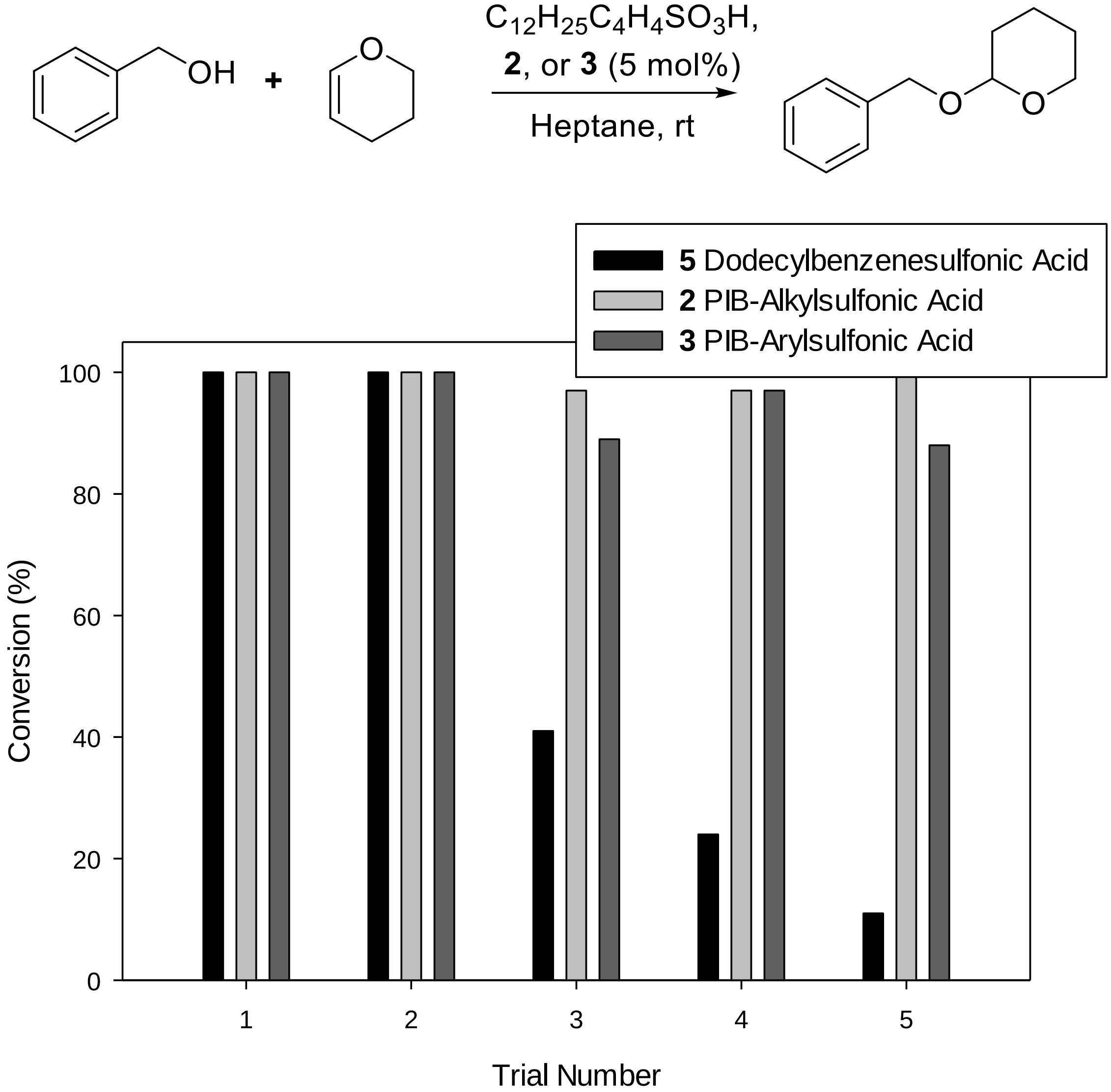


Figure III-16 Conversion of the protections of benzyl alcohol with dihydropyran was tested in recycling experiments with dodecylbenzenesulfonic acid, 2, and 3.

The PIB bound sulfonic acid catalysts **2** and **3** were then added to PAO_{432} and the recyclability of the acid catalysts and the PAO_{432} solvent in this benzyl alcohol protection was examined. The results show that **2** and PAO_{432} or **3** and PAO_{432} could be recycled ten times (Figure III-17). Recycling of each trial was accomplished by allowing the acetal formation to proceed for 1 hour and then pouring the reaction mixture into a centrifuge vial that contained 3 mL of acetonitrile. After mixing, the two phases were centrifuged to separate the solvents, the acetonitrile was then removed by pipette, fresh reagents were added to the PAO_{432} phase, and the reaction was repeated. The acetonitrile phases from the ten cycles were combined and washed twice with heptane to remove any remaining PAO_{432}. Excellent isolated yields of 91% and 90% of the product were obtained using **2** and **3** respectfully. Gratifyingly, neither the PAO_{432} solvent nor the PIB bound acids were present in the isolated product in any detectable amount based on both ^1H and ^{13}C NMR spectroscopic analysis of the products that showed no peaks due to either PIB or PAO.

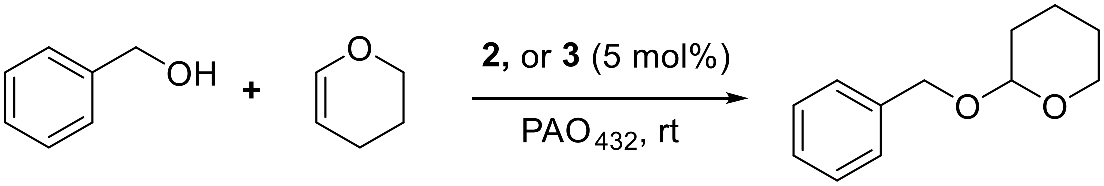


Figure III-17 PIB bound acids 2 **and** 3 **in PAO_{423} are effective catalysts for the dihydropyran protection of benzyl alcohol and can be recycled 10 times without noticeable lost in yield or contamination of the product by catalyst or solvent.**

Next, I tested **2** and **3** in PAO_{432} in a multicomponent reaction (MCR) to form a 3,4-dihydropyrimidin-2-one derivative (Figure III-18). This reaction was modeled on prior work by Li and coworkers[89] who showed that 30 mol% methanesulfonic acid could catalyze the combination of urea, benzaldehyde and acetoacetate in refluxing ethanol to form this heterocyclic product. In my case, I used 3 mmol of urea, 2 mmol of benzaldehyde and 2 mmol of acetoacetate in 10 mL of PAO_{432} and carried out the reaction at 90 °C. Reactions were carried out using 25 mol% of either **2** or **3** and the final product from 7 cycles was isolated in 80% and 81% yield using **2** and **3** respectively.

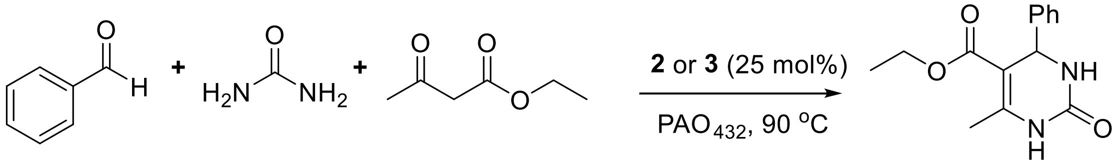


Figure III-18 Multicomponent reaction of 2 mmol of benzaldehyde, 3 mmol of urea, 2 mmol of ethyl acetoacetate in 10 mL of PAO$_{432}$ catalyzed by either 2 **or** 3 **at 90 °C.**

In this process, the substrate was first added to the PAO$_{432}$ phase. However, while the benzaldehyde and the ethyl acetoacetate readily formed a 0.2 M solution, the urea solid did not appear to dissolve. Separate experiments showed that urea is essentially insoluble in PAO$_{432}$ and only marginally soluble in heptane. However, prior work by others has shown that adding 0.1-2 M of cosolvents changes the microenvironment for dyes in heptane or PAO and I hypothesized that the 0.2 M benzaldehyde and ethyl acetoacetate that are soluble in PAO$_{432}$ at 25 °C could have similar effects and solubilize at least some of the urea at 90 °C. Gratifyingly, I found that in this MCR we were indeed able to use the highly polar urea substrate in PAO$_{432}$. Unlike the acetal formation described above, the product in this case was insoluble in PAO$_{432}$. Thus when the reaction was complete, the product could be isolated from the catalyst-containing PAO$_{432}$ phase by pouring the product slurry into a centrifuge tube and centrifuging the suspension for 10 minutes at 1000 rpm. The catalyst-containing PAO$_{432}$ phase was then decanted back into a reaction vessel. After addition of fresh substrates, the reaction could be repeated. This recycling was carried out 7 times. Then the solid product from all 7 reactions was combined and the product was recrystallized from ethanol. The recrystallized product was isolated by filtration. However, this initial product did contain traces of PAO_{432} based on ^1H NMR spectroscopy. Thus, it was washed with two 5-mL portions of heptane. After drying, the isolated product was free of PAO_{432} by ^1H NMR spectroscopy. The isolated yields of product were 82% and 81% for reactions catalyzed by **2** and **3** respectively.

I next studied both **2** and **3** in esterification reactions. Esterifications were of particular interest to us for several reasons. First, as noted above esterifications are an equilibrium process. While the ester and water are normally slightly favored in a reaction of a carboxylic acid and water, the equilibrium constants are not much greater than one. Thus, traditional approaches to esterification rely on using an excess of one reagent or the use of some sort of scheme to separate water continuously. The former approach is exemplified by esterifications with simple alcohols like methanol or ethanol where one uses a large excess of the alcohol, discarding the excess reagent after the reaction. Alternatively, in reactions of these or larger alcohols that involve stoichiometric ratios of substrates, these esterifications are driven to completion by the use of a Dean-Stark trap and refluxing toluene to remove water or by the use of other water trapping agents like zeolites. I reasoned that the use of PAO_{432} might be able to drive the reaction by excluding the water as it formed. This would be an improvement over these traditional approaches and might allow the use of stoichiometric amounts of carboxylic acid and alcohol. Second, esters are typically more volatile than the carboxylic acids that are used to form them. Thus, I thought this could be a good way to show the advantage of low volatility polymeric solvents like PAO_{432} in separations as we could simply distill the product esters from reaction mixtures at reduced pressure which would allow for a simple workup and subsequent recycling of the reaction media and unreacted carboxylic acid.

First, we sought to determine if catalysts like **2** or **3** in PAO_{423} would be effective in esterifications by comparing their reactivity with that of a more traditional catalyst like *p*-toluenesulfonic acid in a traditional non-recyclable solvent like toluene (Figure III-19). Gratifyingly, both **2** and **3** in PAO_{432} give comparable rates to the more traditional conditions of *p*-toluenesulfonic acid in toluene.

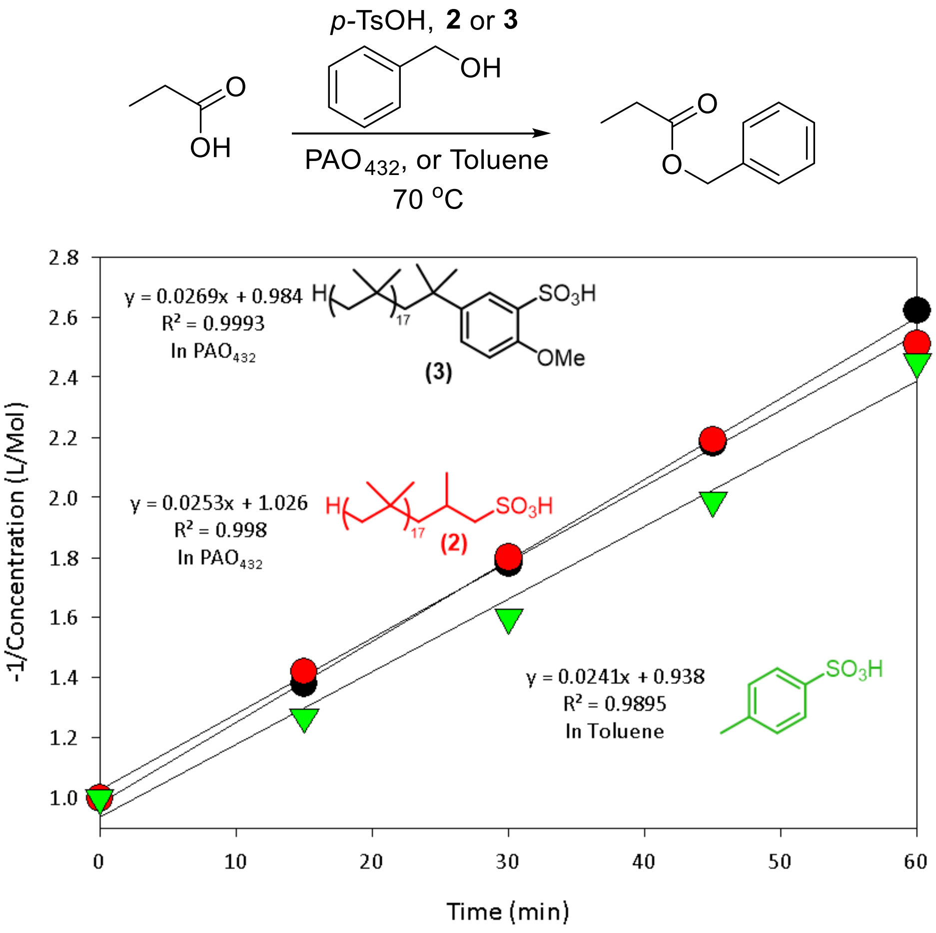


Figure III-19 Comparison of kinetics for esterification of propionic acid with benzyl alcohol using 2 or 3 in PAO_{432}, or *p*-toluenesulfonic acid in toluene at 70 °C.

The conversions of carboxylic acids and alcohols to esters was then examined using **2** or **3** as catalysts with a variety of acids and alcohols using 10 mmol of acid, 10 mmol of alcohol with 1 mol% of the catalyst in PAO_{423} at 70 °C (Table III-2 and Table III-3). Esterifications generally proceeded in good yield even using this 1:1 stoichiometric ratio of carboxylic acid and alcohol with this modest catalyst loading.

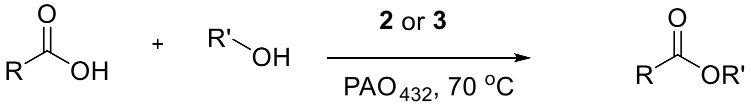


Table III-2 Alcohol to ester conversions using catalyst 2 **in PAO_{423} at 70 °C with calculated theoretical conversions in parentheses.**

Catalyst **2**	Acetic Acid	Hexanoic Acid	Octanoic Acid
Methanol	94% (84%)	88% (73%)	89% (55%)
Ethanol	83% (77%)	97% (78%)	95% (69%)
Propanol	87%	80%	81%
Benzyl Alcohol	77%	81%	65%

Table III-3 Alcohol to ester conversions using catalyst 3 **in PAO_{423} at 70 °C with calculated theoretical conversions in parentheses.**

Catalyst **3**	Acetic Acid	Hexanoic Acid	Octanoic Acid
Methanol	94% (84%)	91% (73%)	91% (55%)
Ethanol	89% (77%)	95% (78%)	84% (69%)
Propanol	86%	93%	80%
Benzyl Alcohol	80%	87%	73%

In the case of the methyl and ethyl ester products in Table III-2 and Table III-3 above, we also compared the observed results with catalysts **2** and **3** in PAO_{432} with a theoretical value for this esterification. This theoretical value was calculated based on the heats of formation of these methyl and ethyl ester products, the starting alcohols, carboxylic acids and water. The values for the heats of formation for these methyl and ethyl esters, the starting alcohols, carboxylic acids, and water are all readily available from NIST.

$$\Delta H = \Delta_f H^o_{ester} + \Delta_f H^o_{water} - \Delta_f H^o_{acid} - \Delta_f H^o_{alcohol}$$

Equation III-1 Calculation of ΔH using heats of formation for alcohol, acids, esters, and water.

$$\Delta G = \Delta H - T\Delta S \approx \Delta H$$

Equation III-2 Approximation of ΔG as ΔH assuming that the TΔS term is small.

$$Keq = e^{\frac{\Delta G}{RT}}$$

Equation III-3 Equation for calculating an equilibrium constant from ΔG.

$$Keq = \frac{[ester][water]}{[alcohol][acid]}$$

Equation III-4 Equation for calculating Keq from equilibrium concentrations.

$$[ester] = \frac{1}{1 + \sqrt{\left(\frac{1}{Keq}\right)}}$$

Equation III-5 Equation for calculating equilibrium concentration of the product ester from an equilibrium constant

In these calculations, the ΔH^o_f(alcohol), ΔH^o_f(acid), ΔH^o_f(ester), and ΔH^o_f(water) were used to calculate a ΔH for the reactions forming the methyl and ethyl esters (Equation III-1). If we assume the entropy term for these reactions is small then ΔH should be a good approximation of ΔG for the reaction (Equation III-2). Using this approximation of ΔG we calculate the expected equilibrium constant for the reactions that formed methyl and ethyl esters (Equation III-3). This equilibrium constant can be converted into a solution concentration for the product ester (Equation III-5) using Equation III-4, which can then be used to give a conversion in a stoichiometric reaction. These calculated conversions are also shown in Table III-2 and Table III-3 in parentheses. In all cases the experimental value for the conversion of the alcohol to ester was better than the theoretical value, confirming in part that our PAO_{432} and polymer bound acid system could be used to give good conversions of alcohols to esters even when using stoichiometric amounts of the carboxylic acid. We ascribe this difference to the self-separation of water from the PAO_{432} phase. However, this effect is still modest. That may be due to the 1M alcohol and 1M carboxylic acid polarizing the PAO_{432} phase to some extent – polarization that reduced the extent of exclusion of water. While results are inconclusive, this notion is supported by the differences between our observed conversions and the theoretical ones which are greatest for the lipophilic reactions involving octanoic acid.

I chose the formation of the methyl ether of hexanoic acid (Figure III-20) as a test reaction to examine recycling of catalyst and solvents in these esterifications, recycling our acid/solvent system via vacuum distillation of the product. This product has a high enough boiling point to be easily separable from water, and any remaining alcohol which distill off first, while also being still significantly lower than the boiling point of hexanoic acid, allowing for clean separation of the product ester from both the lower boiling alcohol and water as well as the higher boiling carboxylic acid. In a typical reaction, 10 mmol of hexanoic acid and 10 mmol of methanol were allowed to react in 10 mL of PAO_{432} at 70 °C with 1 mol% of either **2** or **3**. After 5 hours, the water and excess alcohol were removed at reduced pressure. Then the product was isolated by vacuum distillation. The product distilled at 135 °C as the pure ester which was free of contamination by methanol, hexanoic acid, the catalyst **2** or **3**, and PAO_{423} based on ^{1}H and ^{13}C NMR spectroscopic analysis. The flask was then charged with fresh methanol and hexanoic acid and the reaction was repeated 5 times with either **2** or **3** to give 80% and 81% isolated yields of methyl hexanoate with catalysts **2** and **3** respectively.

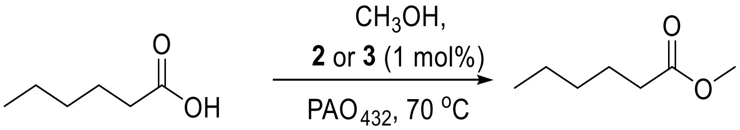


Figure III-20 Esterification of hexanoic acid and methanol in PAO_{432} at 70 °C using 1 mol% of either 2 **or** 3

Conclusion

Two PIB bound sulfonic acid catalysts **2** and **3** were synthesized and shown to be effective in a PAO_{432} solvent in three different types of reaction. The PIB bound acids were both shown to be more recyclable in a conventional heptane system than the commercially available dodecylbenzenesulfonic acid when used to catalyze a benzyl alcohol DHP protection reaction. This PIB bound acids **2** and **3** in PAO_{432} could be reused for 10 cycles in good yields when using extractions by a polar solvent such as acetonitrile to remove the polar product. Even highly polar reagents such as urea could be used in these acid/polymer solvent systems to give good yield of dihydropyrimidin-2-

one derivatives by filtration of the precipitate product and subsequent recrystallization of the product. This reaction demonstrated the PAO_{432} was superior to heptane as a recyclable solvent, as some of the heptane would be lost during heating and centrifugation. Esterification reaction rates were determined for PAO_{432} with either **2**or **3** and these rates were comparable to traditional *p*-toluenesulfonic acid/toluene. Our system however holds the distinct advantage of being able to be separated and recycled by vacuum distillation of the product, whereas the toluene system would be distilled under these conditions. These acid/PAO_{432} systems have also been shown to give improved conversions of the starting alcohol to the ester product when compared to computed theoretical values. We ascribe this higher conversion to the extrusion of water from the solvent which helps to drive the reaction by Le Chatelier's Principle.. Finally, the products isolated from these reactions were free of any PAO_{432} or polymer bound acid contaminant, showing that this system can be used recyclability in a variety of reactions to give pure products.

CHAPTER IV

STUDIES ON THE RECYCLABILITY OF PIB BOUND ROSE BENGAL

Introduction

Singlet oxygen ($^1O_2$) is an ideal green reagent for the generation of peroxide because it can be sustainably sourced from molecular oxygen. Moreover, in many of its reactions it behaves as an atom economical reagent with both oxygens of a singlet oxygen reactant being incorporated into the product. $^1O_2$ generated from ground state triplet oxygen by photosensitizers has found broad use in a variety of applications including photooxidations, photodynamic therapy of cancer, and even in polymer science.[90] There are numerous types of photosensitizers for generation of $^1O_2$. These include transition metal complexes, porphyrins, and even semiconductors. For instance, 5,10,15,20-tetraphenyl-21*H*,23*H*-porphine (PTT) was used to generate singlet oxygen in the synthesis of Spiroiminodihydantoin (Figure IV-1). After the $^1O_2$ reacted with 8-oxoG the product was reduced by dimethyl sulfide and allowed to warm to room temperature, Spiroiminodihydantoin was produced in good yield. While there are many types of $^1O_2$ generating materials, my limited studies described in this chapter focused on the use of organic dyes for singlet oxygen generation.

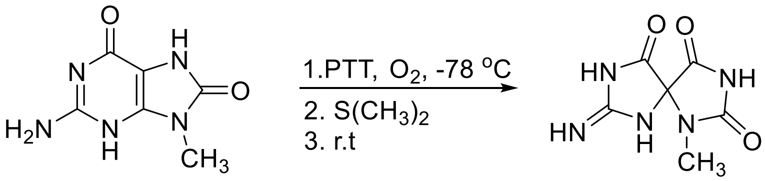


Figure IV-1 Conversion of 8-oxoG to Spiroiminodihydantoin using PTT to generate singlet oxygen

Examples of dyes capable of catalyzing the formation of $^1O_2$ include Rose Bengal, Eosin Y, and Methylene Blue (Figure IV-2). These photosensitizer dyes have been used for a variety of different purposes. For instance, Methylene Blue, and Violet Crystal among others have been studies on silicon oxide surfaces to use their singlet oxygen generation for antimicrobial applications.[91] Methylene Blue and Rose Bengal have also been studied in nanoparticles for their potential use in phototherapy.[92]

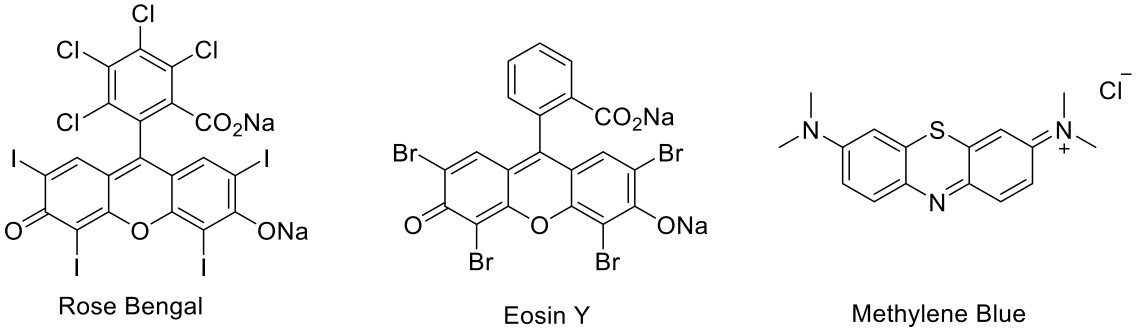


Figure IV-2 Some photosensitizers dyes

These dyes have also been used to generate singlet oxygen for organic reactions. For instance, Rose Bengal was used to generate singlet oxygen in the final step of the total synthesis of Dysidiolide (Figure IV-3).[93] This final step involved selective oxidation of a furan ring, showing that under low temperature conditions, singlet oxygen can be selective.

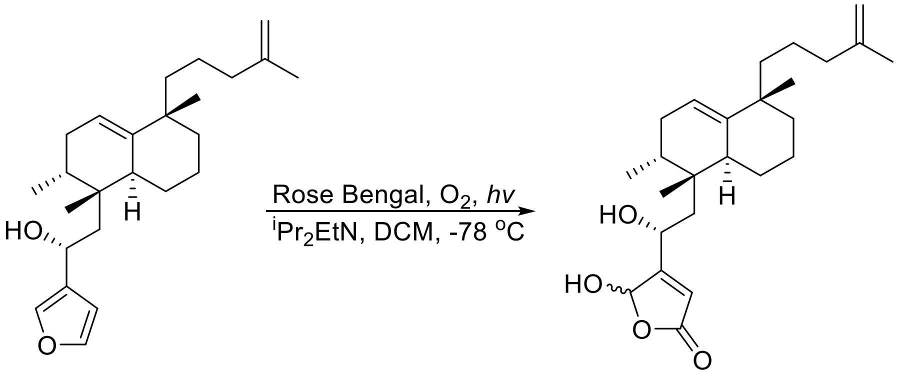


Figure IV-3 Use of Rose Bengal in the final step of the total synthesis of Dysidiolide.

Eosin Y has also been used to convert oxygen to $^1O_2$. For example, it was used in the photooxidation of a variety tri-arylphosines to the corresponding phosphine oxides (Figure IV-4).[94]

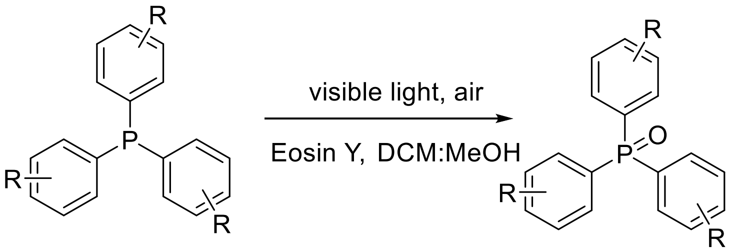


Figure IV-4 Use of Eosin Y as a photocatalyst for the oxidation of phosphines to phosphine oxides. R groups include 4-methyl, 3-methyl, 4-methoxy, 4-ethyl, 4-chloro, 4-^{t}butyl, 4-nitrile, 4-fluoro, and 4-trifluoromethyl.

Steenken and coworkers[95] have shown that Methylene Blue, in the presence of light and oxygen converts phenol to hydroquinone and benzoquinone in modest amounts

(Figure IV-5). They additionally noted the selectivity of this process, as the other isomeric products, such as catechol and resorcinol are not observed.

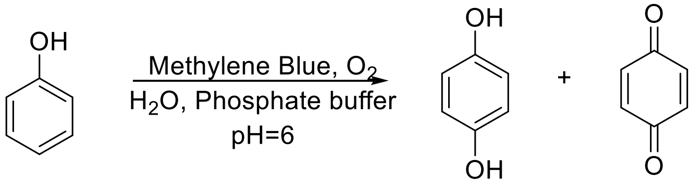


Figure IV-5 Methylene Blue generated $^1O_2$ converts phenol to hydroquinone and benzoquinone.

While many dyes are available, we chose to focus on the use of a polymer bound Rose Bengal dye. This dye was chosen for several reasons. First, it is commercially available and relatively inexpensive. Second, it has a carboxylate functional group which we hypothesized would be simple to attach to our desired polymer. Third, Rose Bengal is known to catalyze a variety of organic reactions including C-C, C-N, C-O and C-S bond formations[96] this makes it particularly appealing, as a recyclable version of this catalyst could be used for a variety of different purposes and is thus more likely to find widespread use. Fourth, this dye has already been used as a polymer supported dye on supports such as ionic liquids,[97] porous organic polymer,[98] and polystyrene,[99] so this would allow for interesting comparisons of this dye in other solvents and other types of supports.

Results and Discussion

Our hypothesis was that a PIB bound singlet oxygen catalyst in either heptane or PAO would make a useful recyclable catalyst for generation of $^1O_2$. As shown earlier in this dissertation, as well as numerous other papers from within our group, PIB is a versatile nonpolar phase anchor for polar catalysts and dyes.[100,101]

Because the Rose Bengal is a bulky nucleophile, and PIB iodide is a sterically encumbered electrophile, a convergent synthesis was used to attach the PIB to the Rose Bengal using an undecanoate ester linker (Figure IV-6). First, PIB_{1000} alkene **3** was converted into a PIB alcohol **4** via a known hydroboration-oxidation chemistry discussed in an earlier chapter. Second, 1-bromo-undecanoic acid **1** was converted to a 1-iodo-undecanoic acid **2** using a known Finkelstein reaction. The 1-iodo-undecanoic acid **2** was then converted to the PIB bound 1-iodo-undecanoate ester **5** using literature coupling conditions. This PIB bound undecanoate ester **5** could then be attacked by the Rose Bengal nucleophile **6** by heating both together in a biphasic system of heptane:DMF to 90 °C. This further facilitated a simple removal of the unreacted Rose Bengal by separation of the two layers after cooling, which allowed for unreacted dye to be recycled.

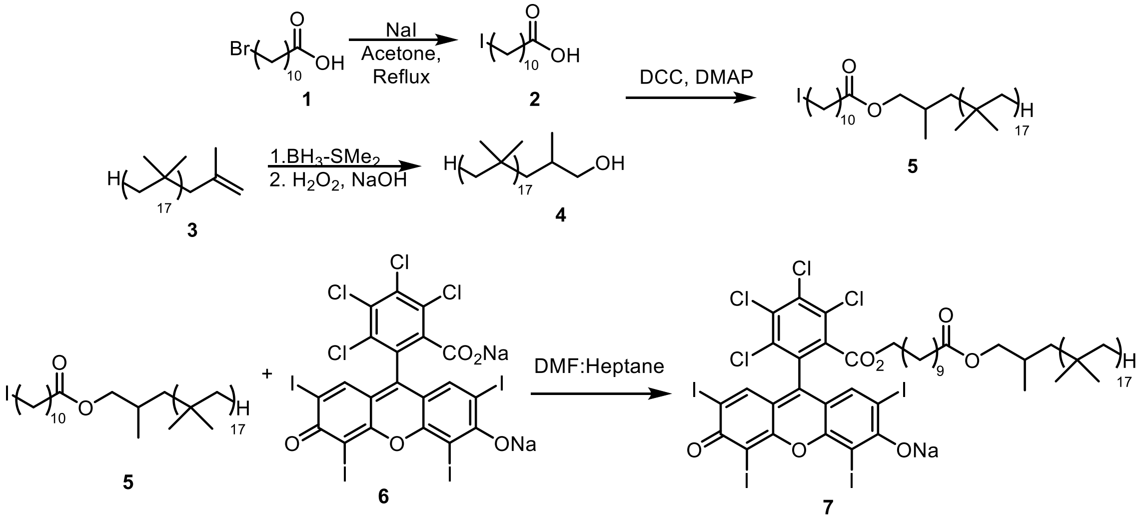


Figure IV-6 Synthesis of PIB bound Rose Bengal

The virgin Rose Bengal **6**, and PIB bound rose Bengal **7** were then tested for their solubility (Figure IV-7) in a heptane and aqueous ethanol co-solvent system. As expected, the virgin Rose Bengal is preferentially soluble in the aqueous ethanol, while the PIB bound Rose Bengal **7** is preferentially soluble in the nonpolar heptane layer. While **7** is preferentially soluble in the heptane phase, there is still some visible leaching of this material into the aqueous ethanol. This is likely due to the large polar end group facilitating leaching of the shorter PIB chains as discussed in the previous chapter with the PIB bound sulfonic acids. This leaching however was minimal so we chose to continue with testing our catalyst for its recyclability in heptane as well as in PAO and DCM. These two comparative solvents would allow us to determine the effect of the polarity of the recycling solvent on both the reaction, and the recoverability of the photocatalyst **7**.

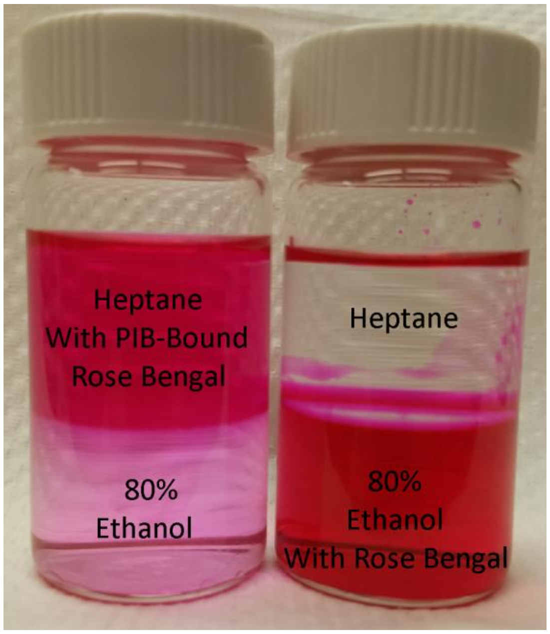


Figure IV-7 (Left) PIB bound Rose Bengal dissolved into heptane above a layer of 80% ethanol: 20% water. (Right) A heptane layer above a layer of 80% ethanol:20% water that contains unbound Rose Bengal.

Our reaction of choice to test the feasibility of this catalyst was a [2+4] cycloaddition of $^1O_2$ to terpinene in a Diels-Alder like reaction. This reaction was chosen because the polar ascaridole product was likely to be easily removed from nonpolar solvents. Additionally, conversion of this material could be easily measured in solution by comparison of the peak integration for the alkene protons in the starting material relative to those of the alkene protons in the peroxi-product.

In order to optimize the effectiveness of this catalyst in a nonpolar heptane phase, four reactions were run in tandem using different methods of introducing oxygen (Figure IV-8). In the all four reactions, 100 mg of terpinene was added to a 1 mg/mL solution of the PIB bound rose Bengal catalyst in 10 mL of heptane. For the first reaction, the flask was left open to allow air to enter and the reaction solution was stirred vigorously to increase surface area. In the second reaction, an air balloon was used to bubble air though solution using a long needle. Two inflated balloons were bubbled through the solution to introduce oxygen, and the flask was sealed with a rubber septum. A third balloon was attached to the flask using a needle to keep the solution under a slight positive pressure of air. For the third reaction, the same process as above was used, however balloons of oxygen were substituted for balloons of air. For the fourth reaction, the laboratory air-line was connected to a gas dispersion tube and air was allowed to bubble through the solution in an uncapped round bottomed flask.

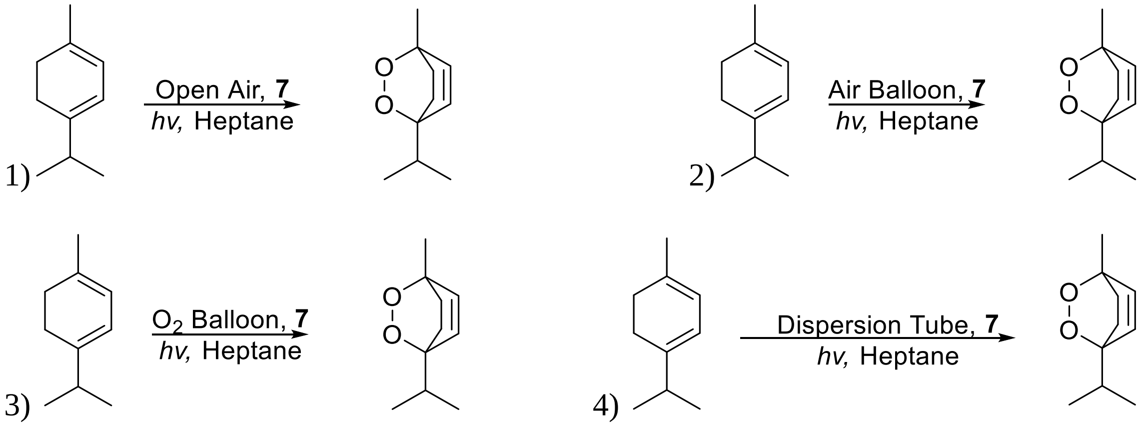


Figure IV-8 PIB bound Rose Bengal 7 **catalyzed conversion of terpinene to ascaridole in heptane using1) a flask open to air 2) an air balloon 3) an O_2 balloon 4) air through a dispersion tube.**

In experiments using 4 hours of irradiation by a 23 watt cfl equivalent bulb, the open air stirring setup gave the highest conversion, followed by the air balloon. However, in experiments 3 and 4 we could visibly see that these solutions had already begun to lose their pink color. This is likely due to photobleaching of the catalyst.

Because of this, the open air stirring was decided on as the reaction condition of choice as it gave the best conversion without visual photobleaching.

These reaction conditions were then tested using several solvents, DCM, EtOH:heptane, Heptane, PAO_2, PAO_4, and PAO_{10} (Figure IV-9 and Figure IV-10). The results show that nonpolar solvents such as heptane and PAO form this dioxygen containing product at a rate similar to that seen in the more polar solvent systems of EtOH:heptane, and DCM. This shows that the polarity of the solvent does not have a large effect on the rate of the reaction.

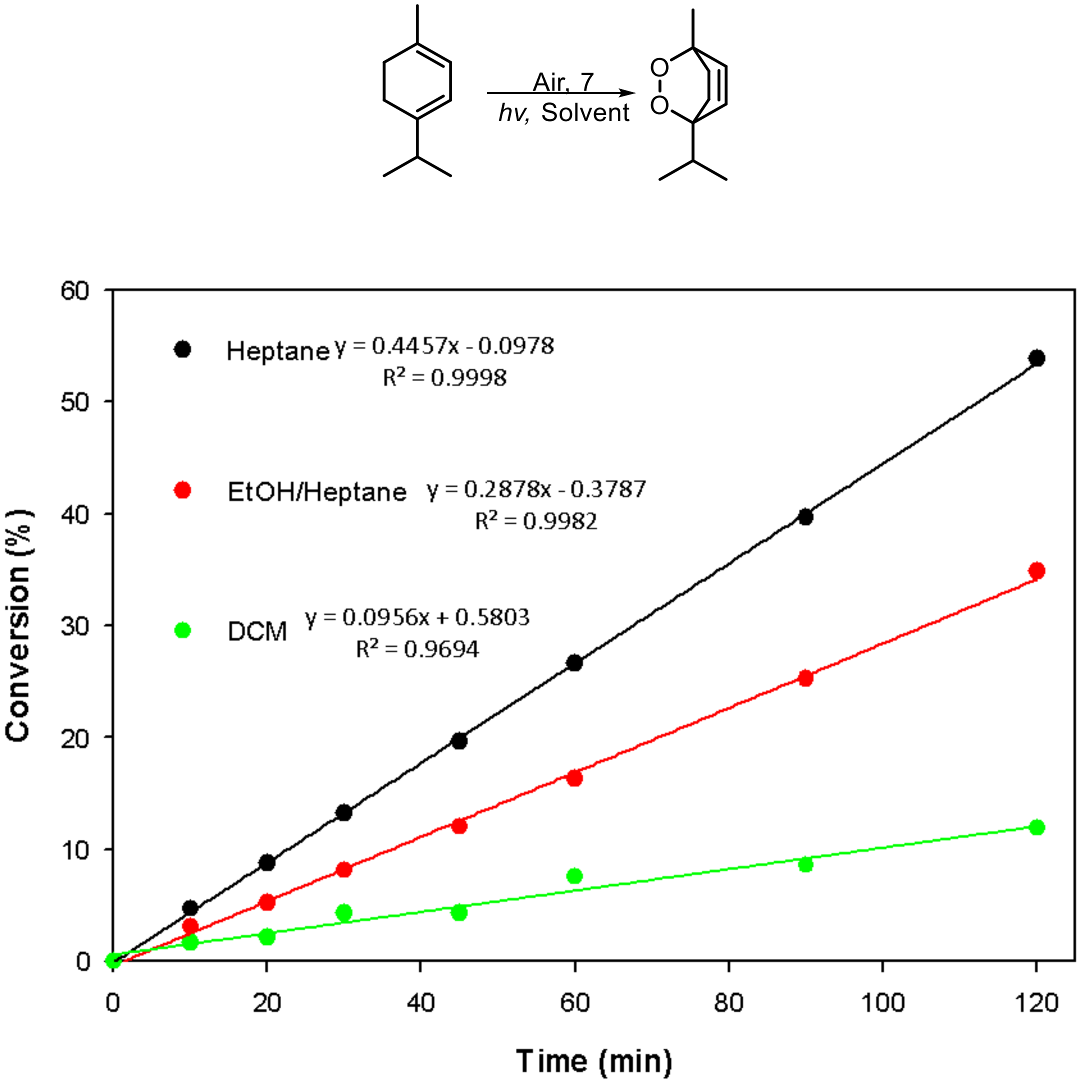
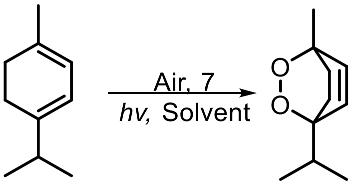


Figure IV-9 Rate of PIB bound Rose Bengal 7 **catalyzed conversion of terpinene to ascaridole in solvents of different polarities.**



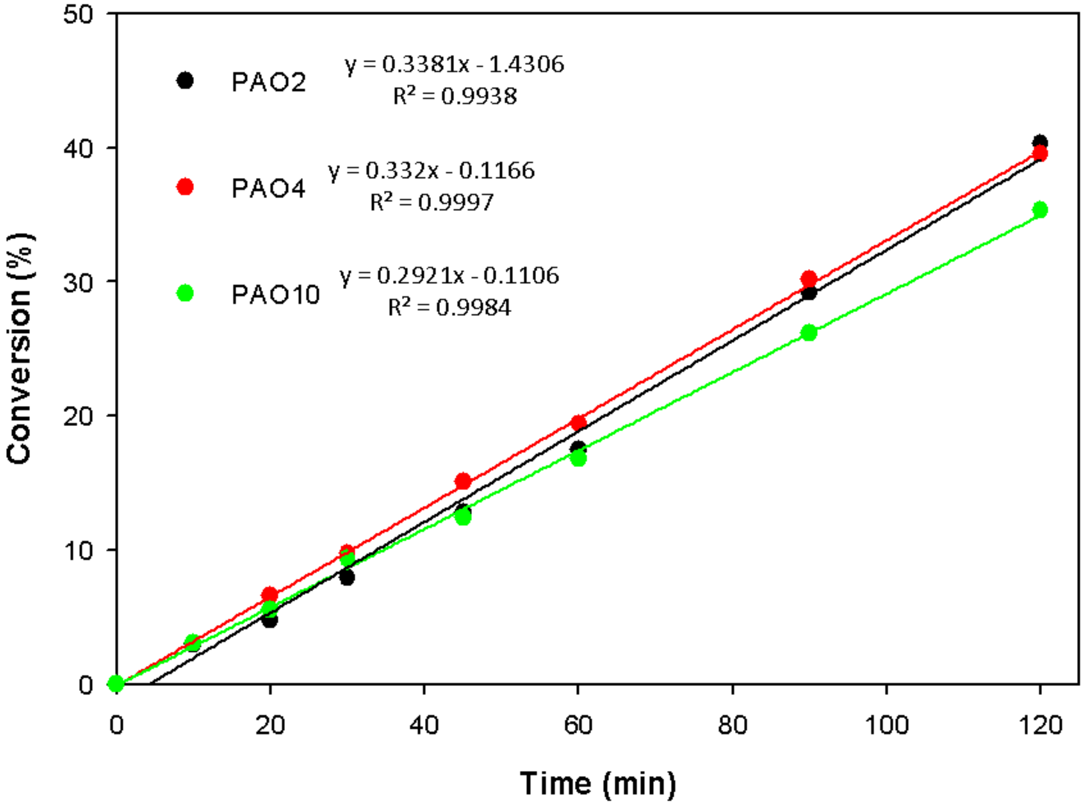


Figure IV-10 Rate of PIB bound Rose Bengal 7 **catalyzed conversion of terpinene to ascaridole in PAOs of different molecular weights.**

Four of these solutions were then tested for their recyclability (Table IV-1). The 100 mg of terpinene dissolved into the stated solvent with 10 mg of the PIB bound Rose Bengal **7** and allowed to stir in an open flask for 4 h while being irradiated with a 23 watt cfl bulb. After 4 h, a sample was take and used to obtain a ^{1}H NMR spectrum to assess conversion. After 4 h, the remainder of the reaction solutions of heptane, DCM and PAO_4 were extracted with 80% ethanol (aq) to remove the product. In the case of the EtOH:heptane system, 1 mL of water was added to separate the latent biphasic system. The organic phase was then charged with fresh terpinene and additional solvent was added for the heptane and DCM to replace solvent loss to evaporation and leaching into the aqueous phase. Heptane had to be added to the heptane:EtOH solution to replace losses due to evaporation and leaching and a fresh 5 mL of ethanol was also added. The process was repeated 2 times.

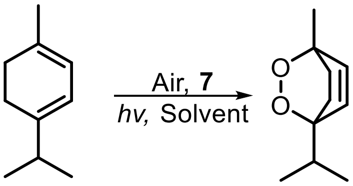


Table IV-1 Conversions of terpinene to ascaridole in various recycled solvents.

	Heptane	EtOH:Heptane	DCM	PAO_4
1st Use	98%	89%	32%	76%
2nd Use	96%	91%	13%	21%
3rd Use	16%	98%	10%	4%

The results show a wide variation in the recyclability of this PIB bound catalyst. In heptane, while the conversions were initially good, there was a rapid decline in conversion after the second trial, with the catalyst being significantly photobleached by the third trial. Additionally, more solvent had to be added to the second and third trials to maintain the same solution concentration. In heptane:ethanol, the conversions of the terpinene were relatively constant. A potential problem in this case is that the volatile nature of the solvent led to solvent loss during the open air reactions. In these cases, additional solvent had to be added to the system in order to maintain the reaction concentration. This was even more of a problem for the DCM which had significant solvent loss due to the volatility of the solvent. Additionally, photobleaching of the catalyst in the DCM solvent appeared to be more rapid, leading to relatively poor conversions of the terpinene. In this case too, solvent had to be added after each reaction trial to maintain the reaction solution concentration. For the PAO solvent, the catalyst appears to photobleach more readily than in heptane.

Subsequent studies by a colleague – Dr. Ying-Hua Fu have shown that the PAO used does contain a contaminant. Thus, it would be worthwhile to reexamine this latter system with PAOs that do not contain this impurity. These studies were carried out with the collaboration of an undergraduate – Peyton Young – and at the end of the 10-week term it became apparent that the catalysts may not have been stored properly over the timeframe of the experiments, making inadvertent photobleaching another potential cause of the difference between the heptane and PAO experiments.

Conclusion

A nonpolar phase soluble PIB bound Rose Bengal **7** was synthesized. **7** is phase selectively soluble in heptane and PAO. Experiments showed that this dye could be dissolved in either of these hydrocarbons, DCM or in a homogeneous heptane/EtOH mixture. In the case of PAO, an extraction of this solution with acetonitrile showed that most of the dye was retained in the PAO phase. Similar results were seen with heptane in an extraction with aqueous ethanol and in the latent biphasic heptane/EtOH solution where the PIB bound dye was again retained in the hydrocarbon phase. Good conversions of terpinene to ascaridole were also seen in reactions where this PIB bound dye was used to generate singlet oxygen. However, studies with heptane, heptane/EtOH and PAO suggest that the catalyst undergoes significant photobleaching when generating $^1O_2$. Additionally, even in a sealed vial, the stock solution of catalyst slowly degrades over weeks due to this photobleaching, showing that while the solvent and the PIB bound species may be recoverable, the catalyst itself degrades significantly over time. However, this decomposition could be minimized by storing the dye solutions in the dark. These initial studies did suggest that a recycling may be possible, but again the results are inconsistent with PAO solutions behaving anomalously vis-à-vis their heptane counter parts. Thus some additional studies need to be carried out to determine if this dye could be a useful recyclable dye using a PIB phase anchor and a recyclable PAO solvent.

CHAPTER V

EXPERIMENTAL

General Experimental

PAOs were obtained from Exxon-Mobile, Cheveron Philips Chemical, or Ineos. Polyisobutylene was obtained from either BASF or Texas Polymer Corporation. All other materials were purchased from commercial sources and used without further purification unless otherwise stated.^{1}H NMR spectra were recorded on Inova NMR spectrometers operating at 300 MHz, and 500 MHz or a Bruker NMR spectrometer operating at 400 MHz. Chemical shifts were reported in ppm with reference to $CHCl_3$ at 7.26 ppm. ^{13}C NMR spectra were recorded on Inova spectrometers operating at 75 MHz and 125 MHz or Bruker NMR Spectrometers operating at 100 MHz. Chemical shifts are reported in ppm with reference to $CHCl_3$ at 77.00 ppm. Coupling constants are given in Hz and the spin multiplicities are indicated by the following symbols: s (singlet), d (doublet), t (triplet), dd (doublet of doublets), br (broad peak) and m (multiplet).

Syntheses and Experimental Procedures

NMR Spectroscopic Studies of Depolymerization of Terminally Functionalized Polyisobutylene Oligomers

In the general procedure for initial depolymerization studies in toluene using ^{1}H NMR spectroscopy, the PIB_{1000} substrate (1 g, 1 mmol) was dissolved in 6 mL of toluene. Then (0.2 mL, 2.2 mmol) of triflic acid was added, and the resulting mixture was allowed to stir for 20 h at 25 °C. A 1 mL aliquot of the solution was then removed and passed through a silica-packed glass pipet to remove triflic acid. The eluent was then concentrated using a rotary evaporator at a reduced pressure, and the residue was dissolved in $CDCl_3$ for ^{1}H spectroscopic analysis. The extent of depolymerization was analyzed by measuring the integral of the signal for the *tert*-butyl group of 4-*tert*-butyltoluene at 1.3 ppm that was seen when depolymerization occurred. When the integral of the residual poly(isobutylene methylene) protons in the isobutylene repeating units due to the unreacted PIB_{1000} derivative at 1.42 ppm was calibrated to 2, the percent conversion to 4-*tert*-butyltoluene could be calculated using Equation V-1.

$$\%Conversion = (integral\ at\ 1.3\ ppm) * \frac{100}{9 + integral\ \ at\ 1.3\ ppm}$$

Equation V-1 Equation to calculate the conversion of polymer to depolymerization products

GPC Studies of Low-Temperature Depolymerization Reactions

PIB_{1000} alkene (1.0 g, 1 mmol) was dissolved in benzene (6 mL) and placed in an ice bath. After being allowed to cool (some benzene freezing occurred), triflic acid (0.2 mL, 2.2 mmol) was added, and aliquots were removed at noted times and passed through silica as described above. The aliquots were then reduced via a reduced pressure and diluted with THF to 25 mg/mL, and GPC data were acquired.

GPC Studies of Depolymerization of Polyisobutylene Oligomers with Different End Groups

Functionalized PIB_{1000} (1.0 g, 1 mmol) was dissolved in benzene or toluene (6 mL), and triflic acid (1.0 mL, 11 mmol) was added. This mixture was allowed to stir for 20 h at room temperature. A 1 mL aliquot was then taken and passed through silica as described above. This sample was then diluted with THF to 25 mg/mL, and GPC data were acquired.

GPC Studies of Depolymerization of PIB_{1000} Alkene in Concentrated Benzene Solutions

PIB_{1000} alkene (1.0 g, 1 mmol) was added with benzene (either 0.8 mL, 9 mmol or 1.6 mL, 18 mmol) and triflic acid (0.2 mL, 2.2 mmol). This was then stirred for 18 h at 25 °C, passed through a silica plug, and diluted in THF to 25 mg/mL, and GPC data were acquired

Synthesis of PIB_{1000} Alcohol

PIB_{1000} alkene (50 g, 50 mmol) was dissolved in 100 mL of hexane. Borane dimethyl sulfide solution (8.5 mL, 85 mmol) was added, and the resulting solution was stirred for 24 h. The reaction flask was then cooled to 0 °C, and 40 mL of ethanol was added. 12 mL of 4 N NaOH (aq) was then added followed by dropwise addition of 8 mL of 35% hydrogen peroxide. The reaction mixture was stirred for 2 h, and then 100 mL of water was added. The organic phase was then separated and washed with water and brine. The organic phase was then dried with sodium sulfate and concentrated under a reduced pressure to give 45 g (90%) of the product PIB_{1000} alcohol was obtained (residual hexanes were present): ^{1}H NMR: 0.87−1.5 (m, 95H), 3.33 (dd, J = 6.9, 10 Hz, 1H), 3.50 (dd, J = 6, 10 Hz, 1H).

Synthesis of PIB_{1000} Iodide

PIB_{1000} alcohol (10 g, 10 mmol), imidazole (1 g, 15 mmol), iodine (3.5 g, 13 mmol), and triphenylphosphine (3.5 g, 13 mmol) were dissolved in 100 mL of dichloromethane and stirred overnight. The reaction solution was concentrated under a reduced pressure, redissolved in hexanes, and washed with DMF and aqueous ethanol. The organic phase is then dried with sodium sulfate and concentrated under a reduced pressure to give 9 g (90%) of PIB_{1000} terminated with an iodo group (residual hexanes were present): ^{1}H NMR: 0.87−1.5 (m, 240H), 3.15 (dd, J = 6.9, 9.7 Hz, 1H), 3.28 (dd, J = 3.6, 9.7 Hz, 1H).

Synthesis of PIB_{1000} Methyl Ketone

PIB_{1000} alkene (11 g, 11 mmol) was dissolved in 50 mL of pentane and cooled to −78 °C. Ozone was then bubbled through the solution until it turned blue. Then, excess tributylphosphine (4.5 mL) was added, and the mixture was stirred for 3 h. The solution was then washed with aqueous ethanol, dried with sodium sulfate, and concentrated under a reduced pressure to give 9.8 g (89%) of PIB_{1000} terminated with a methyl ketone group (residual pentane was present): ^{1}H NMR: 0.87−1.5 (m, 205H), 2.16 (s, 1H), 2.48 (s, 1H).

Synthesis of PIB_{1000} Carboxylic Acid

PIB_{1000} methyl ketone (6.9 g, 6.9 mmol) was dissolved in 200 mL of THF. Iodine (6.9 g, 54 mmol) was added. Potassium hydroxide (25 g, 440 mmol) was dissolved in 200 mL of water. Tetrabutylammonium bromide (1.6 g, 5 mmol) was then added, and the resulting mixture was allowed to stir overnight. At that point, the reaction solution was concentrated under a reduced pressure, dissolved in hexanes, and washed with DMF, aqueous ethanol, and water. The organic phase was then dried with sodium sulfate and concentrated under a reduced pressure to give 5.7 g (83%) of the PIB_{1000} carboxylic acid-terminated oligomer product (residual hexanes were present): ^{1}H NMR: 0.86−1.5 (m, 334H), 2.34 (s, 2H).

Synthesis of PIB_{1000} Phenol

PIB_{1000} alkene (10 g, 10 mmol) and phenol (19 g, 220 mmol) were dissolved in 100 mL of dichloromethane. The solution was cooled to 0 °C, and 6 mL of concentrated sulfuric acid was added slowly. The solution was then stirred overnight and concentrated under a reduced pressure, and the residue was redissolved in 300 mL of hexanes. The organic solution was then washed with aqueous ethanol and dried with sodium sulfate to give 9 g (90%) of a PIB_{1000} oligomer product terminated with a 4- hydroxyphenyl (phenol) group (residual hexanes were present): ^{1}H NMR: 0.86−1.5 (m, 334H), 6.77 (d, J = 8.4 Hz, 2H), 7.24 (d, J = 8.4 Hz, 2H).

Synthesis of PIB$_{1000}$ Anisole

PIB$_{1000}$ alkene (15 g, 15 mmol) was dissolved in 32 g of anisole. Nine milliliters of concentrated sulfuric acid was added, and the reaction solution was stirred overnight. The solution was then washed with aqueous 1 N NaOH, extracted with hexanes, and washed three times with acetonitrile. The organic phase was then dried with sodium sulfate and concentrated under a reduced pressure to give 16 g (>100%) of PIB$_{1000}$ oligomer terminated with a 4-methoxyphenyl group (residual hexanes were present): ^{1}H NMR: 0.86−1.5 (m, 209H), 1.82 (s, 2H), 1.86 (s, 6H), 3.82 (s, 3H), 6.85 (d, J = 9.0 Hz, 2H), 7.29 (d, J = 9.0 Hz, 2H).

Depolymerization of PIB$_{1000}$ Alkene in the Presence of 2.2 Equivalents of Triflic acid in 60 mL of Toluene

PIB$_{1000}$ (1.0 g, 1 mmol) was dissolved into 60 mL of toluene and triflic acid (0.2 mL, 2.2 mmol) was added at 25 °C and the resulting mixture was to stir the stated time. Aliquots of the solution were then passed through a silica plug and diluted with THF to 25 mg/mL. GPC data were then acquired

Depolymerization with Excess Equivalents of Triflic Acid in 60 mL of Benzene for PIB$_{450}$, PIB$_{1000}$, or PIB$_{2300}$

PIB with a specific molecular weight (1.0 g, 1 mmol) was dissolved into 60 mL of benzene and 1.0 mL of triflic acid was added at 25 °C and the resulting mixture was allowed to stir for 20 h. The solution was then washed with water to remove the acid, and a sample was taken and diluted for GPC analysis.

PIB_{1000} Hydrogenation

PIB_{1000} alkene (2 g, 2 mmol) was dissolved in a mixture of 25 mL of heptane and 25 mL of ethanol. Palladium on activated charcoal (10%) (100 mg, 5 mol%) was added and the system was purged with hydrogen. After being placed under a hydrogen balloon, the reaction solution was allowed to stir overnight. The product solution was then filtered and concentrated at reduced pressure to give 1.8 g (90%) of hydrogenated PIB_{1000} that did not contain any vinyl hydrogens or allylic hydrogens even when gain for the 4-5.5 δ and 2-3 δ regions of the spectrum gain were increased (vide infra).

Synthesis of PIB-Bound Alkylsulfonic Acid 2

Alkene terminated polyisobutylene 1 (10 g, 10 mmol) ($M_w = 1000$) was dissolved in a 50:50 mixture of heptane and ethanol (200 mL) in a 250-mL round-bottomed flask. To this was added azobisisobutyronitrile (0.165 g, 1 mmol) and thioacetic acid (2.15 mL, 30 mmol). The reaction mixture was then irradiated overnight with a 254-nm UV lamp. After stirring overnight, water (50 mL) was added to induce biphasic separation of this latent biphasic solvent mixture. The aqueous phase was separated, and the organic phase was washed 3 times with 50-mL portions of 90% aqueous ethanol. The organic phase was then concentrated under reduced pressure and the resulting viscous residue was dissolved in 100 mL of

THF in a 250-mL round-bottomed flask. This thioester was then hydrolyzed and oxidized using 35% hydrogen peroxide (3.7 mL) and 88% formic acid (23 mL). This reaction mixture was stirred overnight at 60 °C. After stirring overnight, the reaction mixture was concentrated under reduced pressure and the residue was dissolved in 100 mL of heptane. This heptane solution was then washed 3 times with 50-mL portions of acetonitrile and concentrated to give 5.1 g of a viscous brown oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.67 (br, chemical shift is concentration dependent), 3.23 (dd, J = 3.7, 14.2 Hz, 1H), 3.00 (dd, J = 8.9, 14.2 Hz, 1H), 2.18 (br, 1H), 0.84-1.6 (m).

Synthesis of PIB-Bound Arylsulfonic Acid 3

Anisole-terminated PIB (10 g, 10 mmol) was prepared using the above procedure. The product of this synthesis was dissolved in dichloromethane (100 mL) in a 250-mL round-bottomed flask. The reaction flask was then charged with 20% fuming sulfuric acid (10 mL). This mixture was stirred overnight and then concentrated under reduced pressure. The viscous oily residue was dissolved in heptane (100 mL) and washed with 3 times with 50-mL portions of acetonitrile to remove residual sulfuric acid. The heptane phase was then concentrated under reduced pressure to give 7.4 g of a viscous purple oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, J = 2.2 Hz, 1H), 7.59, 7.02 (dd, J = 8.8, 2.2 Hz, 2H), 3.82 (s, 3H), 3.76 (br, chemical shift is concentration dependent), 1.80 (s, 2H), 0.84-1.6 (m).

Recycling of PAO/Acid in the Dyhydropyran Protection of Benzyl Alcohol

Benzyl alcohol (108 mg, 1.0 mmol) and 3,4-dyhydro-*2H*-pyran (DHP) (101 mg, 1.2 mmol) were dissolved in PAO_{432} (10 mL) containing .05 mmol of **2** or **3**. The reaction mixture was stirred at room temperature for 1 h. The reaction mixture was then placed into a test tube, and acetonitrile (3 mL) was added. The resultant biphasic mixture was then thoroughly mixed and then separated by centrifugation for 5 min at 1000 rpm. The acetonitrile and PAO_{432} layers were then separated using a pipette. The PAO_{423} phase containing the PIB-bound acid **2** or **3** was recycled by addition with fresh alcohol and DHP. This process was carried out 10 times with no measurable loss of the PAO solvent. The acetonitrile phases from these 10 cycles were then combined, washed twice with 5-mL portions of heptane, and then concentrated to give an average isolated yield of 91% and 89% for **2** and **3** respectively. ^1H NMR (400 MHz, $CDCl_3$) δ 7.41-7.29 (m, 5H), 4.82 (d, J = 12 Hz, 1H), 4.72 (t, J = 3.4, 1H), 4.53 (d, J = 12 Hz, 1H) 4.00-3.92 (m, 1H) 3.63-3.55 (m, 1H) 1.94-1.54 (m, 6H).

Comparison of Acid Recyclability in the 3,4-dyhydro-2*H*-pyran Protection of Benzyl Alcohol

Benzyl alcohol (108 mg, 1.0 mmol) and 3,4-dyhydro-2*H*-pyran (DHP) (101 mg, 1.2 mmol) were dissolved in 10 mL of heptane containing .05 mmol of **2**, **3**, or **5**. This solution was stirred at room temperature for 1 h. After 1 h, a small aliquot of the heptane phase was dissolved in $CDCl_3$ and the conversion was determined by

^{1}H NMR spectroscopy. The remaining heptane was extracted with 5 mL of acetonitrile to separate the product, from heptane. The heptane phase containing the acid catalysts **2**, **3**, or **5** was charged with fresh alcohol and DHP and the process was repeated for 5 cycles.

Recycling of PAO/Acid in a Multicomponent Synthesis of 3,4-Dihydropyrimidin-2-one

Benzaldehyde (212 mg, 2 mmol), ethyl acetoacetate (260 mg, 2 mmol), and urea (180 mg, 3 mmol) were dissolved in 10 mL of PAO_{432} in a capped vial. Then 0.5 mmol of either **2** or **3** was added. The resulting mixture was then stirred at 90 °C for 12 h. Then the mixture was transferred to a centrifuge tube and centrifuged for 5 min at 1000 rpm. The PAO_{432} and acid were then decanted and reused in a subsequent reaction cycle with fresh reagents. The solid product and excess urea were from all 7 cycles was combined and recrystallized from ethanol to remove excess urea. The recrystallized 3,4-dihydropyrimidin-2-one was then washed twice with 5-mL portions of heptane to remove any residual. The product was isolated in average isolated yield of 82% and 81% for **2** and **3** respectively. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (br, chemical shift is concentration dependent, 1H), 7.35-7.29 (m, 5H), 5.53 (br, chemical shift is concentration dependent, 1H), 5.43 (dd, J = 2.5 Hz, 1H), 4.1 (dq, J = 2.5, 7.3 Hz, 2H), 2.38 (s, 3H), 1.19 (t, J = 7.3 Hz, 3H), mp = 201-203 °C.[24]

Rate Comparison for Esterification of Propionic Acid with Benzyl Alcohol using 2, 3, and *p*-toluenesulfonic Acid

Propionic acid (740 mg, 10 mmol) and 10 mmol of benzyl alcohol (1.08 g, 10 mmol) were dissolved in 10 mL of PAO_{432} (using 0.1 mmol of **2** or **3** as a catalyst) or in toluene (using 0.1 mmol of *p*-TsOH as a catalyst). The reaction was then stirred at 70 °C. Aliquots of the reaction were removed periodically and analyzed by ^1H NMR spectroscopy. The conversion percentage was determined from the integration ratio of the alcohol protons at 4.6 δ and the ester protons at 5.0 δ.

General Esterification Procedure

A carboxylic acid (10 mmol) and an alcohol (10 mmol) were added to a 20-mL vial and dissolved in PAO_{432} (10 mL) containing 0.1 mmol of either **2** or **3**. The vial was then capped, and the reaction mixture was heated to 70 °C and stirred for 5 h. After 5 h, an aliquot was taken, and dissolved in $CDCl_3$. The conversion of starting material to product was then determined by comparison of the integral of the alcohol for singlets at ca. 4.6 δ or 3.4 δ (benzyl alcohol and methanol, respectively), triplet at ca. 3.6 δ (propanol) and quartet at ca. 3.7 (ethanol) and the ester proton singlet at ca. 5.0 δ and 3.6 δ (benzyl esters and methyl esters, respectively), triplet at ca. 4.1 δ (propyl esters) and quartet at ca. 4.1 δ (ethyl esters) using ^1H NMR spectroscopy.

Recycling of PAO/Acid in the Esterification of Hexanoic Acid with Methanol

Hexanoic acid (1.16 g, 10 mmol) and methanol (320 mg, 10 mmol) were dissolved in PAO_{432} (10 mL) in a 25-mL round-bottomed flask. Then 0.1 mmol of either **2** or **3** was added. The reaction was carried out at 70 °C for 5 h. After 5 h, the product was isolated and purified by vacuum distillation at reduced pressure. The remaining solution of PAO_{432} and the catalyst was charged with fresh hexanoic acid and methanol and the procedure was repeated. This process was repeated 5 times, affording methyl hexanoate with an average isolated yield of 80% and 81% for **2** and **3**, respectively. ^1H NMR (400 MHz, $CDCl_3$) δ 3.60 (s, 3H), 3.23 (t, J = 7.6 Hz, 2H), 1.59-1.52 (m, 2H), 1.3-1.19 (m, 4H), 0.83 (t, 3H).

Synthesis of PIB-Bound 11-Iodoundecanoate

11-Bromoundecanoic acid (5 g, 18.9 mmol) was dissolved in 25 mL of acetone. To this was added (6.5 g 40 mmol) of sodium iodide. The resulting mixture was then refluxed overnight. After reflux, the mixture was cooled and 50 mL of water was added to precipitate the product. The precipitated product was then be isolated by vacuum filtration. The product was recrystallized in hot ethanol to give 3.7 g of 11-iodoundecanoic acid. 1.9 g of this resulting 11-iodoundecanoic acid (m.p.=59-62 °C) was then dissolved into 150 mL of DCM. To this was added 5.2 g PIB alcohol which was made as described above, 50 mg of DMAP, and 1.2 g of DCC. The resulting reaction mixture was stirred overnight. The reaction solution was then washed with saturated $NaHCO_3$ (aq.) and the DCM was then removed at reduced pressure. The resulting slurry was dissolved into 50 mL of hexanes, and washed with 20 mL of acetonitrile 3 times. The hexanes solvent was then removed under reduced pressure to give 3.1 g of the PIB bound iodoundecanoate. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.96 (dd, J = 6, 9 Hz 1H), 3.81 (dd, J = 6, 9 Hz 1H) 3.2, (t, *J* = 7.2 Hz, 2H), 2.343 (t, *J*= 7.5 Hz, 2H), 1.86-1.0 (m, 190H).

Synthesis of PIB bound Rose Bengal

The PIB bound iodoundecanoate (0.5 g, 0.38 mmol) synthesized above was dissolved in 80 mL of a 1:1 mixture of heptane and DMF in a round-bottomed flask. Rose Bengal (0.4 g, 0.41 mmol) was then added to the reaction solution. The solution was then heated to 90 °C and allowed to react overnight. Upon cooling the layers were separated and the heptane was washed with 50% ethanoic water. The heptane layer was then removed under reduced pressure to give 0.62 g of the PIB bound Rose Bengal (71% yield) as a viscous purple oil.

Rose Bengal Catalyzed Conversion of Terpinene to Ascaridole

Terpinene (100 mg, 0.74 mmol) was dissolved into 10 mL of heptane. Other solvents including a 50:50 mixture of heptane:ethanol, DCM, PAO_2, PAO_4 and PAO_{10} were also examined. Then 10 mg of the PIB bound Rose Bengal (0.5 mol%) was added. The resulting mixture was left open to the air and stirred for 5 h while it was irradiated with a 23 watt compact fluorescent lamp lightbulb. The reaction solution was then washed with 60% ethanol (aq.) to remove the product. The heptane, heptane:ethanol, DCM, or

PAO_4 solution of the catalyst was then reused in a subsequent trial. The conversion of starting material to product was then determined by comparison of the integral of the alkene doublet at ca. 6.5 δ and 5.6 δ using ^1H NMR spectroscopy.

CHAPTER VI

CONCLUSION

In summary, the work presented in this dissertation describes the recycling of PIB species and their use in PAO solvents. The PIB and PAO oligomers are commercially available, and inexpensive. These oligomers are both selectively soluble in nonpolar media like heptane, DCM, and THF and insoluble in polar solvents. This gives them excellent recyclability. The recyclability of both of these species was tested in three separate ways.

In the first approach, PIB was recycled by a depolymerization process. PIB with suitable end groups was depolymerized by triflic acid in the presence of an arene solvent. In the presence of weaker acids, there was no appreciable amount of depolymerization. When arene solvents such as toluene and benzene were used, the depolymerization products - *tert*-butylarenes - were formed rapidly. The polymer chain was completely depolymerized within five minutes. When more electron rich arenes such as anisole were used, the depolymerization process was inhibited presumably due to a solvent leveling effect due to the fact that the acid present – a protonated arene – was less acidic versus protonated benzene or protonated toluene . When less electron rich arenes like chlorobenzene were used, the depolymerization reaction slowed or did not occur due to the solvent being a poor nucleophile. These acid catalyzed depolymerizations were also carried out at sub-ambient temperatures. These experiments showed that the depolymerization is complete in 5 min even at 0 ℃. Additionally, this depolymerization occurred even in the presence of 0.1 equivalents of solvent relative to the end group. These more concentrated reactions also formed larger amounts of the di-*tert*-butylbenzene and when a large excess of benzene was used. These depolymerizations were shown to be end group dependent, and were end group driven. This was confirmed by the use of a hydrogenated PIB that did not undergo depolymerization under our conditions. Suitable end groups for this depolymerization included alkenes, arenes like anisole and phenol, and alcohols when a large excess of the acid was used. Unsuitable end groups were those that cannot readily be removed via protonation to give a tertiary carbocation including end groups such as iodides, carboxylic acids, and ketones. This depolymerization process was slowed by dilution, however this process showed no increase in retention time in the GPC spectra. This showed that the individual chains are slower to begin depolymerizing at lower concentration, but once the chain was protonated, it completely depolymerized within minutes. Depolymerization of PIB of molecular weights 450, 1000, and 2300 Da shows that this depolymerization goes to the same *tert*-butylbenzene regardless of the size of the initial polymer. This process was shown to be energetically favorable both by observation and mathematically in three different ways using the enthalpy of the reactants, products, and heats of reactions in both the liquid and gas phase.

The second recycling study explored using PIB bound sulfonic acid catalysts that were anchored in a recyclable PAO solvent. These catalysts were initially tested for their recyclability by comparing them to the commercially available dodecylbenzenesulfonic acid. Two PIB bound acids and dodecylbenzenesulfonic acid were used in the DHP protection of benzyl alcohol in heptane as a solvent. These studies showed that in heptane, the PIB acids were more recyclable than the dodecylbenzenesulfonic acid. These PIB bound sulfonic acids were then dissolved into PAOs and used to catalyze three different reactions. In the first, the PIB-bound sulfonic acids were used as recyclable catalysts in the DHP protection of benzyl alcohol 10 times. The products in this case were separated from a PAO solution of the catalyst using a liquid/liquid extraction with acetonitrile. In the second reaction, the PIB bound acids were used in a multicomponent reaction to form a 3,4-dihydropyrimidin-2-one derivative. In these reactions, the product was separated by filtration and the acid/solvent system could be reused at least 7 times without loss of product yield. This reaction showed that even polar reagents such as urea can be used in this PAO/acid solvent system, at least when other polar reagents are present. Finally, these acids were tested in esterification reactions. Both PIB-bound sulfonic acids were shown to give better conversion of alcohol to and carboxylic acid to ester product when the starting materials were used in a 1:1 stoichiometric ratio than expected based on a theoretical calculation of the equilibrium constant for this esterification reaction. This improved conversion in the case of a PIB catalyst in a PAO solvent was attributed to the nonpolar nature of the PAO solvent which excluded water from the reaction and thus drove the equilibrium to form products according to Le Chatelier’s principle. These PIB-bound sulfonic acid/PAO systems could also be recycled after being used in these esterifications 5 times. An additional novel feature of this chemistry was that the methyl hexanoate product could be removed from the acid/solvent system by vacuum distillation to give products free of contamination by the acid catalyst, PAO solvent, or any unreacted carboxylic acid and alcohol.

In preliminary studies, a third example of this chemistry was explored using a Rose Bengal dye that was bound to PIB and dissolved in PAO. This polymer bound singlet oxygen generating catalyst was used in the oxidation of terpinene to ascaridole. Although the products could be easily separated from the catalyst and PAO solvent, the recyclability of the PIB-bound Rose Bengal catalyst in initial studies of this photooxidation chemistry were modest. However, this was likely due to poor storage of the light sensitive catalyst and the photobleaching of the catalyst. These catalysts merit further study in these reactions. As noted in the discussion, storing this catalyst in the dark when not in use, could make this photocatalyst more recyclable.

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